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TRANSLITERATION

There is no ideal system of transliterating Russian, each has its advantages and disadvantages. For the translation of *Geokhimiya* we have chosen the system used by *Chemical Abstracts*, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

EFFECT OF METAMORPHISM ON GEOLOGIC AGE AS DETERMINED BY THE LEAD METHOD

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Abstract

The applicability of the graphic method of calculating the true age of a min- ral and of the time of its last metamorphism, proposed by Ahrens and Veser- l, is described in this article. With this method it has been determined that e true age of Belomore uraninites is 1950 x 10^6 years, not 1800 x 10^6 years s was formerly thought. These changes in the uraninite age were taken into count in calculating a new value for the constant of K-capture by K^{40} accord- g to radiogenic argon included in micas. The newly calculated value proved be equal to 5.4 x 10^{-11} year. This value differs by 10% from the former .02 x 10^{-11} year^{-1}) and differs only by 3% from the value obtained in the U.S.A.

The wide variations in geologic ages obtained from the ratios b^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{207}/Pb^{206}, and Pb^{208}/Th^{232} are related to me sort of a loss either of the initial or of the final products of de- y. Many investigators believe that the emanations of the radioactive inerals are among the principal factors responsible for these riations.

Such is the viewpoint of F. Wickman [1], as is well known. He even sumed that the emanation in question is due entirely to the long-lived otope of radon, whose atoms diffuse through fissures and capillaries. he pointed out, the result is a lower Pb^{206}/U^{238} ratio and a corres- ndingly higher Pb^{207}/Pb^{206} ratio. It has been concluded that the most liable age figure may be obtained from the Pb^{207}/U^{235}, for uranium inerals, even if the mineral is not particularly well preserved. I. E. rik [2] adheres to this reasoning, as he pointed out that emanation the main process by which the isotope ratios are disturbed in radio- tive minerals. Since the emanation of radon for our samples may be preciable, larger than in the case of actinon, the age calculated from Pb^{207}/U^{235} ratio should be the most reliable of all.

The foregoing premises were followed in estimations of the age of aninites from Belomore (The White Sea maritime areas), and the ure of 1800 x 10^6 years, calculated from the Pb^{207}/U^{235} ratio, was cepted as the result.

Many investigators expressed their doubts recently as to emanation ng the sole factor affecting the age estimations. These doubts are ed on the following evidence:

1. It was proved that the deficiency of lead caused by the emanation is smaller than actual losses of this element. This was shown experimentally by Eckelman and Kulp for uranium ores from Lake Athabaska. The same was observed for the Witwatersrand ores and for the Karelian uraninites.

2. It was shown that, in emanation by the minerals, the principal part is played not by diffusion of radon, as was formerly believed, but by effects resulting from losses of the emanating atoms themselves.

This thesis was sustained by the experiments of I. E. Starik and O. S. Melikova [3] who found that the diffusion of radon from uraninite becomes noticeable only above 500°C and is sustained further by the equality of the radon and actinon emanation coefficients established by N. D. Kosov and V. V. Cherdyntsev [4] for certain minerals. If radon and actinon are equal, the most reliable estimates of the age should be made on the basis of the Pb^{207}/Pb^{206} ratio and not from the Pb^{207}/U^{235} ratio, as was formerly believed.

3. We must consider the fact that emanations of the majority of uranium minerals, in natural environments, are considerably below the experimental levels determined in the laboratory. This discrepancy should be favored by pressures in the earth's crust which cause diminutions in porosity, sealing of fissures, and a lowering of permeability.

The evidence here listed leads to the conclusion that emanation cannot be the principal cause of the scattering of the age data obtained by the lead method from different ratios of the isotopes.

Davidson and Bowie, in 1951 [5], were the first ones to suggest metamorphism and redeposition of pitchblende ores. These phenomena may easily explain the large discrepancies in the results by Louw [6] based on different isotopic ratios for the age of the Witwatersrand uranium ores.

Louw's explanation of the discrepancies by losses of radon contradict the fact of the low emanating capacity of his ores, which does not exceed 0.2 to 0.3%. The hypothesis of Davidson and Bowie is confirmed by the accumulation of galena within the altered pitchblende and by the diagnostic isotopic composition of lead in the galena. The Pb^{207} and Pb^{206} isotopes are definitely higher in this galena, or they may be the only two isotopes contained therein. Observation shows convincingly that a galena of this kind could have been formed only by a metamorphism of the pitchblende in later times.

Analogous suppositions were advanced in 1954 by C. B. Collins, R. M. Farquar, and R. D. Russell [7], in order to explain the scattering of the age data on the Athabasca, Canada, uranium ores. In their view, there has been a solution of the ancient ore and its subsequent reprecipitation.

In 1954-1955, A. I. Tugarinov [8] and others gave a very interesting report at the Fourth Session of the Committee on the Absolute Age of Geologic Materials dealing with the forms of lead in uranium pitchblende, in relation to the absolute age of the minerals. The authors deavored to extract selectively sulfides and native lead from pitch- ende without destroying its structures. The presence of relatively gh concentrations of Pb^{206} and Pb^{207} in the galena of the pitchblende ay be taken as convincing proof that the mineral specimens they used d been metamorphosed. The Oldridge-Miller method, first proposed 1929 [9] for the isolation of metallic lead from slag, as subsequently fined by L. E. Gurev [10], Yu. V. Klimenko [11], and others, was nployed by the authors.

The lead sulfide was extracted by trituration of the powdered rock th crystalline iodine, as described by P. M. Isakov [12]. Amounts of dinary and radiogenic lead extracted selectively by iodine from the chblende and the isotopic composition of radiogenic lead were calcu- ed from the isotopic composition of ordinary lead in galena collected the same district. The approximate age of the pitchblende, 250 to 0 million years, was calculated from the isotopic composition of its d by the investigators here cited.

In the same year, A. I. Tugarinov [13] calculated the time of the tamorphism for the Witwatersrand pitchblende from the content of diogenic lead of two samples of galena. His results are chiefly ientation, however, as they were based on the 2 x 10^9 year age of the anium ore which is known to be too low. The corresponding period metamorphism of the ore was estimated at 1300 to 1700 million ars.

In 1955, S. I. Zykov, K. K. Zhirov, V. V. Zhirova, and I. S. Ivanova] found that other radioactive minerals, such as uraninites of rthern Karelia, may also be subject to hydrothermal alterations. e alterations result in losses of fairly large quantities of radiogenic d, some of which becomes precipitated as galena in small cracks in rock. From the isotopic composition of the lead of galena inclu- ns, they estimated the time of metamorphism of the uraninite at 500 700 million years. Phenomena of this kind are very common in ure, and they involve many radioactive minerals. Thus, according Tilton and Davis et al. [15], certain zircons and other minerals are ject to hydrothermal alterations.

The question is: is it not possible to evaluate the effect of this fac- on the age data? Ahrens in 1955 [16] made the first attempt in this ection. He showed that, if the Pb^{207}/U^{235} ratio in different minerals m one and the same locality is plotted on the abscissa and the Pb^{206}/ ^{8} ratio in the same minerals is plotted on the ordinate, the majority he points will fall on a straight line.

The straight line obtained by Ahrens for Rhodesian monazites (Fig. ntersects the curve of the harmonized data ($^tU^{235} = {}^{-t}U^{238}$) at a it corresponding to 2700 x 10^6 years. This datum, according to ens, should be accepted as the true age of Rhodesian monazites. o the explanation of this relationship, Ahrens had offered an im- bable suggestion to the effect that the relationship is connected nuclear processes.

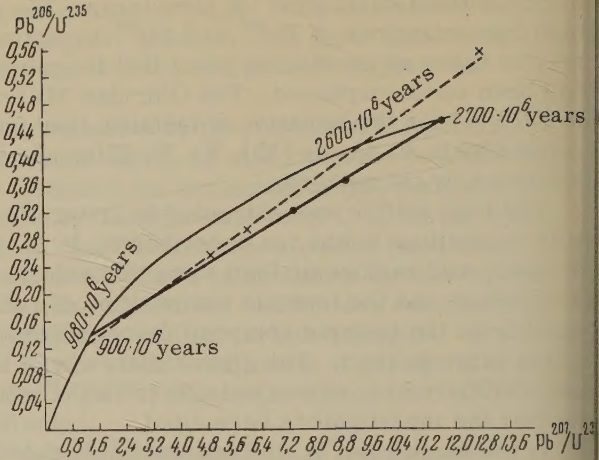

Fig. 1. Bikita, Rhodesia, Africa; Manitoba, Canada

Later on Wetherill [17] demonstrated that the relationship in question depends on losses of lead and uranium that occurred in the past. The time when these losses were taking place may be calculated graphically by extrapolation of the straight line until it intersects the curve of the harmonized data. As was already pointed out, one of the points of intersection enables us to calculate the true age of the mineral. The second point indicates the time of the metamorphism for the given group of minerals. Thus the time of the metamorphism is estimated at 980 x 10^6 years fo the Rhodesian monazites. If, however, the straight line passes throug the origin of the coordinates, it means that the alteration of minerals in the given group has taken place very recently indeed.

The relationship here indicated, however, may be observed only under the following strictly defined conditions:

1. There must be no separation of Pb^{207} from Pb^{206} during metamorphism. This thesis is supported by the experimental data of K. K. Zhirov et al. [18], who proved that the ratio of radiogenic Pb^{207}/Pb^{206} remains constant, in the course of leaching lead from Koiti-Tundra allanite, both in the original mineral and in the leachates. G. Tilton et al. [19] also reported that the Pb^{207}/Pb^{206} ratio remains constant in their leaching experiments.

2. Effects of other factors must be insignificant. Examples of the use of the calculations here discussed are presented diagrammatically in Figures 1 through 6. Let us now examine these diagrams.

Figure 1 shows the results obtained for two specimens of uraninite and one of monazite from Manitoba, Canada [20], together with Ahrens results for Rhodesian monazites. The points fall on a straight line, as may be readily seen.

We find from the intersections of the straight line with the curve of the harmonized data, that the age of the minerals is 2600 x 10^6 years and the time of their metamorphism is 900 x 10^6 years. One point on the straight line and considerably above the curve of the harmonized data represents the specimen of monazite. Its position in the graph may be explained partly by losses of uranium and partly by additions

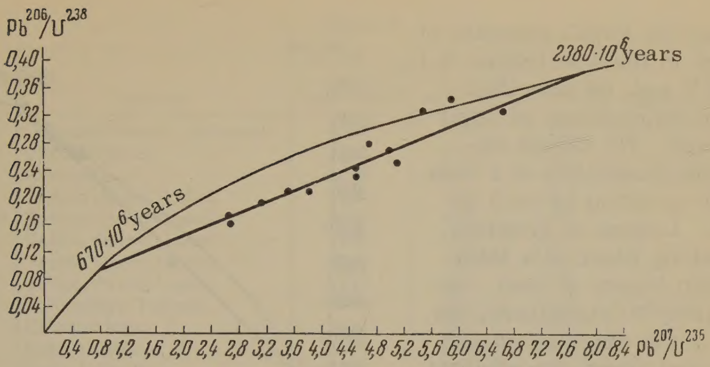

Fig. 2. Witwatersrand uranium ores (according to Louw).

f radiogenic Pb^{207} and Pb^{206} originating possibly in uraninites within e very same pegmatitic vein. One must assume that the alterations f the monazite here discussed were contemporaneous with the metaorphism of the uraninites, 900 x 10^6 years ago.

Figure 2 shows the data for the uranium ores of Witwatersrand [6]. he bulk of the points, with the exception of three, falls on the straight ine. The line intersects the curve of the harmonized data at the point orresponding to 2380 x 10^6 years. This datum refers to the age of e original uranium minerals which were subjected to the hydrotheral alteration. The time of their metamorphism is estimated at 670 x 0^6 years. The Pb^{207}/Pb^{206} ratio in the minerals at the time of their etamorphism is calculated from the slope of the straight line and is und to be 0.178. As we know from the results of Louw, the $Pb^{207}/$ b^{206} ratio in two samples of galena from the same locality is 0.18 and .21 respectively and the origin of this galena is connected with the etamorphism of e uranium ores. ch a coincidence of e results obtained independent methls sustains the reability of the diaams here consucted.

Some of the points ig. 2) lie above the rve of the harmoned data. These dertures from the ear relationship y be due, on one nd, to experimen- error (which is ite probable, if we

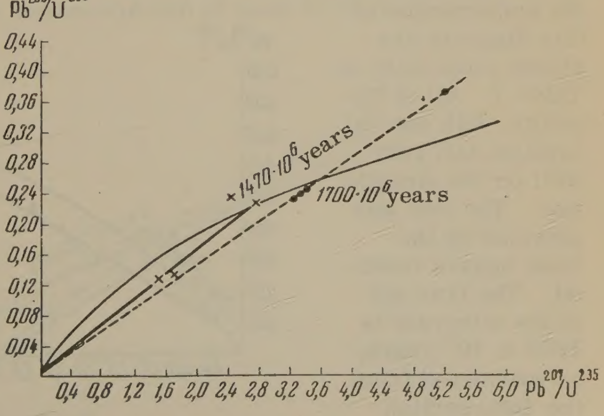

Fig. 3. Rappakivi from Ukraine; Gunnison District, Colorado.

consider the small amounts of uranium in the specimens: 0.1 to 0.3%*) and, on the other hand, to impositions of other processes. We cannot exclude the possibility of a loss of some uranium as well as of lead. Losses of uranium were taking place at a later time than losses of lead. As may easily be visualized, the points in the diagram should be situated above the straight line and even above the curve of the harmonized data, in case of major losses of uranium.

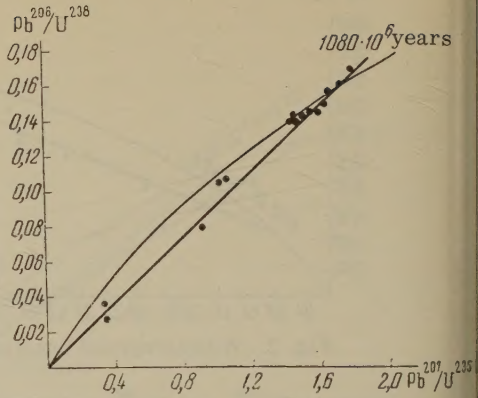

Fig. 4. Wilberforce minerals, Cardiff Township, Ontario, Canada.

Figures 3 and 4 show three examples with the curves passing through the origin of the coordinates. This means that the alteration of the mineral is recent and possibly related to supergene processes. Such processes are also capable of causing severe disturbances of the ratios in the radioactive minerals, as was demonstrated by I. E. Starik and his co-workers [28].

One should think that alterations of this sort took place also in minerals from the Slyudyanka District, Siberia [29], because no lead sulfide could be detected in these minerals even at highest magnifications, of the order of magnitude of 1500X, in conjunction with the fact that the age discrepancies for these minerals, as calculated from different ratios, are very great indeed.

The diagram in Figure 5 representing the data for the radioactive minerals from Belomore and Karelia deserves our special attention. The results used in the construction of this diagram are shown separately in Table 1. All of the points, with one exception, fall very well on the straight line. The line was obtained by the least square method. The true age of the minerals is 1950 x 10^6 years, as calculated from the intersection of the straight line with the

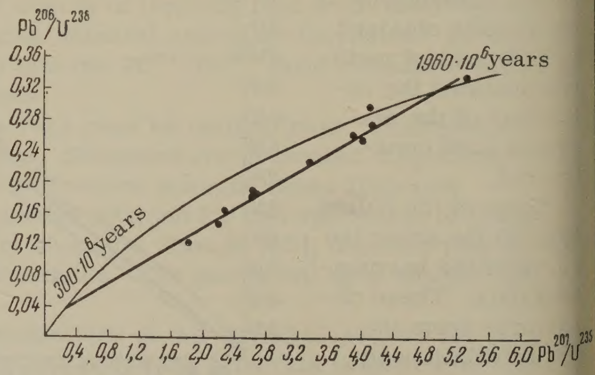

Fig. 5. Belomore.

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*In the original: "0.1 - 3%; 0.1 to 0.3% is meant. VPS

Table 1

ineral	Source	Age, 10^6 years			Authority
		Pb^{207}/Pb^{206}	Pb^{206}/U	Pb^{207}/U^{235}	
onazite	Chernaya Salma, Belomore	1800	1250	1450	K.K.Zhirov [25]
	Chkalov Mine, "	1710	1900	1800	A.A.Avzeiko [26]
	Alakurtti, "	1920	2040	2020	K.K.Zhirov [25]
	Tedino Ozero (Lake), "	1860	1220	1440	
arburan*	Tedino Ozero (Lake), "	1900	1480	1655	
	Tedino Ozero (Lake), "	1850	1250	1460	
	Tedino Ozero (Lake), "	1770	1120	1340	
	Tedino Ozero (Lake), "	1810	850	1170	
raninite	Kamennaya Taibola, "	1870	1760	1800	I.E.Starik et al. [27]
	Chkalov Mine, "	1880	1660	1760	
	Guba Lapsieva, "	1800	1050	1300	
	Guba Lapsieva, "	1780	1150	1380	
	Chernaya Salma, "	1820	1680	1740	

pparently uraniferous asphaltite. EWH

urve of the harmonized data. The error of calculation by the graphic ethod does not exceed ± 50 x 10^6 years. The new datum exceeds the ld by 150 x 10^6 years. The age of the metamorphism equals 300 x 10^6 ears. The Pb^{207}/Pb^{206} ratio in the minerals 300 x 10^6 years ago, at e time of their metamorphism, is 0.132, as calculated from the slope the straight line. As to the ratio of radiogenic Pb^{207}/Pb^{206} in galena om the same district, which is 0.135 according to K. K. Zhirov and I. Zykov [14], it agrees very well with the ratio calculated by me.

One of the points falls above the curve of the harmonized data. This int represents a sample of monazite. The discrepancy here observed ay be explained by a loss of uranium at a later time than the loss of ad, as was explained in the case of the Witwatersrand ores.

Let us turn now to a more complicated case; the uranium ores from the habaska Lake district in Canada. The data are shown diagrammatically Figure 6. As one may see, the points are withing a triangle which may due to twice repeated metamorphism of many of the samples. Let us

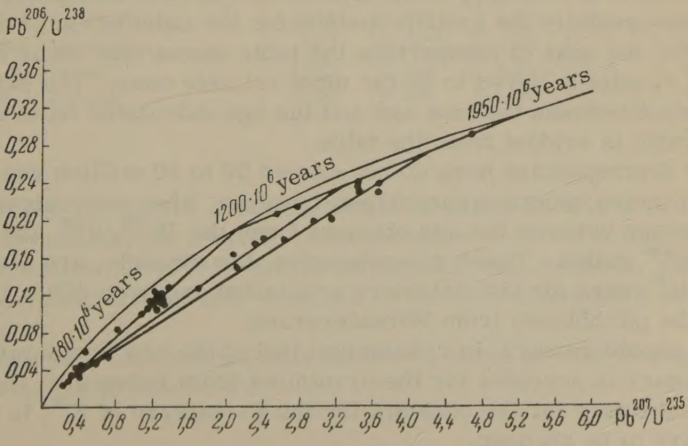

Fig. 6. Saskatchewan, Alberta, Canada.

first draw a line only through the topmost points that lie closest to the curve of the harmonized data. Points representing samples subjected but once to the action of hydrothermal solutions will fall on this line. The alterations in question took place 1200 x 10^6 years ago, as shown by the calculations. Later on, most of the altered samples were metamorphosed for a second time. These twice-metamorphosed samples are situated on the straight lines intersecting the curve of the harmonized data only at one point. The age of the second metamorphism is estimated at 180 x 10^6 years.

It should be noted here that Eckelman and Kulp [21] have already demonstrated that the Athabaska uranium ores were metamorphosed twice, with the calculated age of the first and the second metamorphosis at 1200 and 200 million years ago respectively, as was indicated by determinations involving additions of radiogenic Pb^{207} and Pb^{206} to the test samples of galena and clausthalite from the district. Their results agree very well with my calculated data, and this is convincing proof of the reliability of diagrams constructed for this purpose.

The foregoing examples have one characteristic feature in common: their calculated age is: $Pb^{207}/Pb^{206} > Pb^{207}/U^{235} > Pb^{206}/U^{238}$. According to Eckelman and Kulp, the same relationship is observed in 70% of all age determinations in minerals. In some samples, however, the age relationship is: $Pb^{206}/U^{238} > Pb^{207}/U^{235} > Pb^{207}/Pb^{206}$. Such cases make it impossible to calculate the true age of minerals, because of the scatter-patterns of the corresponding diagram. Such minerals were subjected apparently to far more intricate alterations that cannot be taken into account at this time. These alterations may have been accompanied by losses of large quantities of both uranium and lead, at different times. Monazites investigated by L. V. Komlev and co-workers [22] belong to this category. According to Komlev, the most reliable age datum for such minerals is obtainable from the Pb^{208}/Th^{232} ratio.

Table 2 is a summary of certain cases where it was possible to apply successfully the graphic method for the calculation of the true age. For the sake of comparison the table shows also some experimental results believed to be the most reliable ones. The satisfactory agreement between the true age and the age calculated from the Pb^{207}/Pb^{206} ratio is evident from the table.

The discrepancies here do not exceed 50 to 80 million years. The discrepancies become appreciable, however, when one attempts a comparison between the age obtained from the Pb^{207}/U^{235} and the Pb^{206}/U^{238} ratios. These discrepancies, for example, are already 150 x 10^6 years for the Belomore uraninites and even 400 x 10^6 years from the pitchblende from Witwatersrand.

We should remark, in conclusion, that if the new age datum of 1950 x 10^6 years is accepted for the uraninites from Belomore, the currently accepted figure for the constant for the K- capture of K^{40}, in the USSR, will have to be changed.

Table 2

Source	Determined age, 10^6 yrs.	Method	Age, 10^6 years	Time of metamorphism, 10^6 years
kita, Rhodesia, S.A.	2650	Pb^{207}/Pb^{206}	2700	980
anitoba, Canada	2550	Pb^{207}/Pb^{206}	2600	900
ıpakivi, Ukraine	1725	Pb^{207}/Pb^{206}	1700	Not long ago
ınnison, Colorado, USA	1470	Pb^{207}/Pb^{206}	1470	— —
itwatersrand, Africa	2000	Pb^{206}/U^{238} & Pb^{207}/U^{235}	2380	680
habaska, Saskatchewan, Canada	1900	Pb^{207}/Pb^{206}	1950	1200 and 180
ıreliya, Belomore	1800	Pb^{207}/U^{235}	1950	300
ilberforce, Canada	1100	Pb^{207}/Pb^{206}	1080	Not long ago
ack Hills, USA	1610	Pb^{207}/Pb^{206}	1610	Not long ago
yudyanka, Siberia	480	Pb^{207}/Pb^{206}	500	Not long ago
reat Bear Lake, Canada	1400	Pb^{207}/Pb^{206}	1480	500

This is the consequence of the fact that the age datum of 1800 x 10^6 ears is being used now in the calculations of the K- capture constant r the radiogenic argon in micas. If, however, we take the true age of ese materials into account, the 1950 x 10^6 years, the resulting value ill be 5.4 x 10^{-11} year^{-1}, differing by 10% from the older value but ıly by 3% from the result obtained by the American investigators [24] ıo also had made use of the geochemical method.

Table 3 presents all of the basic data used by myself and by the nericans in calculations of the K-capture constant for K^{40} as well as e results obtained by the calculations. The most reliable average

Table 3

Sample and Source	Age, 10^6 years	Ar^{40}/K^{40}	Calculated λ_K, yrs.$^{-1}$	Used, λ_β, yrs.$^{-1}$
aninite; Portland, Connecticut	267	0.0158	5.51×10^{-11}	4.72×10^{-10}
astonberry, Connecticut	255	0.0156	5.67×10^{-11}	4.72×10^{-10}
ruce-Pine, N. Carolina	375	0.0213	5.20×10^{-11}	4.72×10^{-10}
anchville, Connecticut	367	0.0236	5.82×10^{-11}	4.72×10^{-10}
ıreliya, Belomore	1950	0.183	5.40×10^{-11}	4.72×10^{-10}
öggerite; Ukraine	2100	0.204	5.34×10^{-11}	4.72×10^{-10}

ure for the K-capture constant should be taken as 5.49 x 10^{-11} year^{-1} ırther investigations must be undertaken, in order to refine the K-pture constant for K^{40}, by means of geochemical methods, with the l of the most reliable data obtained by the lead method for uranium nerals.

The following conclusions may be drawn here, by way of a summary the foregoing presentation:

1. The graphic method proposed by Ahrens and Wetherill makes it possible to calculate the true age of a mineral together with the age of its latest metamorphism.

2. Their method is suited to cases in which the age, t_1, is calculated when $Pb^{207}/Pb^{206} > Pb^{207}/U^{235} > Pb^{206}/U^{238}$.

REFERENCES

1. Wickman, F. *Geol. Foren. i Stockh. Forh.* 64, 4, 1942.
2. Starik, I. E. Dopolnenie k Dokladu G. V. Avdzeiko. (Supp. to Report by G. V. Avdzeiko.) *Tr. III Sessii Kom. po Opred. Abs. Vozr. Geol. Form.*, 163 *Izd. Akad. Nauk, SSSR* 1955.
3. Starik, I. E., O. S. Melikova, V. V. Kurbatov, and V. A. Aleksandruk. Zavisimost' Emaniruyushchei Sposobnosti Utaninita po Radonu, Toronu, i Aktinonu ot Temperatury (Dependence of the emanation capacity of urananite for radon, thoron, and actinon on temperature). *Bull. Kom. po Opred. Abs. Vozr. Geol. Form., V.* 1, 33, 1955.
4. Kosov, N. D., and V. V. Cherdyntsev. Emanirovanie Mineralov i Opredelenie Absolyutnogo Geologicheskogo Vozrasta (Emanations of minerals and determination of the absolute geologic age). *Bull. Kom. po Opred. Abs. Vozr. Geol. Form., V,* 1, 22, 1955.
5. Davidson, C. F., and S. H. Bowie *Bull. Geol. Survey Gr. Brit., No.* 3, 1951.
6. Louw, I: D: *South Afr. Min. and Engr. Journ.* 65, No. 3226, 1954.
7. Collins, C. B., R. M. Farquar, and R. D. Russel. *Bull. Geol. Soc. Amer.* No. 65, 1, 1954.
8. Tugarinov, L. I. *Doklady Akad. Nauk.*, 99, No. 6, 1954.

8a. Tugarinov, A. I., L. P. Orlava, S. I. Zykov, and M. S. Chupakhin. O Formakh Nakhozhdeniya Svintsa v Uranievoi Smolke v Svyazi s Opredeleniem Absolyutnogo Vozrasta (On the forms of lead in pitchblende in relation to determination of the absolute age). *Tr. IV Sessii Kom. po Opred. Abs. Vozr. Geol. Form.*, 204, 1957.

9. Oldridge (?) and V. Miller. A method approximating the form of lead in slag and other products of lead blast furnace. (?), 1929.
10. Gurev, A. E. O Forme Soedinenii Svintsa v Shlakakh Svintosovoi Plavki (On forms of compounds of lead in lead smelter slag). *Tsvetnye Metally,* No. 1, 1934.
11. Klimenko, Yu. V. Ratsional *nyi Analiz* (The Rational Analysis). 1938.
12. Isakov, P. M. *Nauchnyi Bull. Leningrad Govt. U.*, No. 23, 1949.
13. Tugarinov, A. I. Ob Opredelenii Vremeni Metamorfizma Izmenennykh Uranovkh Mineralov Metodom Opredeleniya Absolyutnogo Vozrasta (On determination of the time of metamorphism of altered uranium minerals by means of the absolute age). *Bull. Kom. po Opred. Abs. Vozr. Geol. Form., V.* II, 1957.
14. Zykov, S. I., K. K. Zhirov, V. V. Zhirova, and I. S. Ivanov. Opredelenie Vozrasta po Ksenotimu i Uraninitu Zhily Tedino Ozero (Determination of the age by xenotime and uraninite of the Tedino Ozero vein). *Tr. IV Sessii Kom. po Opred. Abs. Vozr. Geol. Form.*, 1957, p 249. Ibid., p. 258: K. K. Zhirov and S. I. Zykov. Izotopnyi Sostav Svintsa Galenitov iz Pegmatitov Severnoi Karelii (The isotopic composition of lead in galena from the North Karelian pegmatites).
15. Tilton, G. R., G. L. Davis, G. W. Wetherill, and L. T. Aldrich. *Trans. Amer. Geophys. Union*, 38, 3616, 1957.
16. Ahrens, L. H. *Geochim. et Cosmochim. Acta (a)* 8, 1, 1955; *(b)* 7, 294, 1955.

17. Wetherill, G. W. *Geochim. et Cosmochim. Acta* 9, 290, 1956. Also in *Trans. Amer. Geophys. Union,* 37, 320, 1956.

18. Zhirov, K. K., S. I. Zykov, and N. I. Stupnikova. O Prochnosti Svyazi Razlichnykh Izotopov Svintsa v Strukture Ortita (On the firmness of binding of different isotopes of lead in orthite structures). *Geokhimiya,* No. 2, 148, 1957.

9. Tilton, G. R., C. Patterson, H. Brown, M. Inghram, R. Hayden, D. Hess, and E. Larsen. *Bull. Geol. Soc. Amer.* 66, 1131, 1955. Also: G. R. Tilton. *Trans. Amer. Geophys. Union,* 37, 224, 1956.

20. Nier, A. O. *Phys. Rev.,* 153, 1939; and *Ibid.* 60, 112, *1941.*

21. Eckelman, W. R., and I. G. Kulp. *Bull. Geol. Soc. Amer.* 67, 35, 1956.

22. Komlev, L. V., S. I. Danilevich, K. S. Ivanova, A. D. Mikhalevskaya, V. G. Savonenkov, and M. S. Filippov. O Vozraste Geologicheskikh Formatsii Yugo-Zapadnoi Chasti Ukrainskogo Dokembriya (On the age of geologic formations of the southwestern part of the Ukrainian Precambrian body). *Geokhimiya,* No. 7, 566, 1957.

23. Gerling, E. K., M. L. Yashchenko, and G. M. Ermolin. Argonovyi Metod Opredeleniya Vozrasta i Ego Primenenie (The argon method of determination of age and its application). *Bull. Kom. po Opred. Abs. Vozr. Geol. Form., V.* II, 1957.

24. Wetherill, G. W., G. I. Wasserburg, L. T. Aldrich, G. R. Tilton, and R. T. Hayden. *Phys. Rev.* 103, 987, 1956.

25. Zhirov, K. K. Doklad na IV Sessii Komissii po Opredeleniyu Absolyutnogo Vozrasta Geologicheskikh Formatsii (Report at the Fourth Sess. of Comm. on determination of the Absolute Age of Geol. Formations). *(In Press.)*

26. Avzeiko, G. V. Rol Izotopnogo Analiza Svintsa v Opredelenii Geologicheskogo Vozrasta (The role of the isotopic analysis of lead in determination of the absolute geologic age). *Tr. III Sessii Kom. po Opred. Abs. Vozr. Geol. Form.,* 153, 1955.

27. Starik, I. E., F. E. Starik, G. A. Avdzeiko, A. Ya. Krylov, A. N. Elizarova, E. N. Bartnitskii, A. V. Lovtsyus, and I. M. Gorokhov. Nekotorye Dannye ob Absolyutnom Vozraste Dokembriiskikh Obrazovanii (Some data on the absolute age of Precambrian formations). *Tr. IV Sessii Kom. po Opred. Abs. Vozr. Geol. Form.,* 1957.

8. Starik, I. E. Forma Nakhozhdeniya i Usloviya Pervichnoi Migratsii Radioelementov v Prirode (Forms and environments of the primary migration of radioactive elements in nature). *Uspekhi Khimii* (Adv. Chem.), *XII,* 288, 1943.

9. Zhirova, V. V., S. I. Zykov, and A. I. Tugarinov. *Geokhimiya, No.* 7, 592, 1957.

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SOME PRELIMINARY DATA ON ELABORATION OF THE POST PRECAMBRIAN SCALE OF ABSOLUTE GEOCHRONOLOGY BASED ON GLAUCONITES

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Abstract

A systematic determination of the absolute geological age of the European part of the USSR and of Czechoslavakia according to glauconites of different age from the Sinian system to the Upper Eocene epoch, except for the Gothlandian and the Triassic systems, has been carried out. The determinations were made out by the potassium-argon method (accuracy ± 10%) on carefully separated monomineralic fractions of glauconites from sands, clays and limestones having been altered by weathering (altogether 23 determinations). Some details of the method are described in the article. The character of argon separation from glauconite with dependence on temperature has been ascertained, which shows that argon begins to separate approximately at a temperature = 300° C, all the argon being practically removed at t° = 500-600° C, (See Fig. 1).

The absolute dating of sedimentary formations is essential in the solution of geologic problems of different kinds. So far, however, there have been no determinations of the absolute age of sedimentary rocks based on authigenic minerals (with the exception of sylvite, whose distribution is very limited).

Development of the argon method has made it possible to use glauconite—an authigenic potassium mineral—in determinations of the absolute age. This opportunity had not been utilized, for all practical purposes, and it was only in 1956 that the first data on the age of some glauconite specimens made their appearance in the literature (Wasserburg, Hayden, and Jensen, [1]; Lipson, [2]). In the USSR, the age of glauconites was determined at the Dagestan Branch of the Academy of Sciences of the USSR by Kh. I. Amirkhanov, K. S. Magataev and S. B. Brandt [3], and by the authors of the present report. Most of the results obtained are in good agreement with the geologic data—evidence of a fairly satisfactory preservation of radiogenic argon in glauconites.

It is possible even now, on the basis of published data, to appraise the high possibilities of the argon method in absolute dating of sedimentary rocks, with utilization of glauconites. It is necessary, however, to undertake certain special studies in order to explain the series of cases in which the age data are abnormally high or abnormally low, to investigate experimentally the mobility of potassium and argon in crystal structures of glauconites, to investigate the mineralogy of glauconites in detail, together with the environments of formation of glauconite, in connection with the indicated possibility of using glauconite as an indicator of geologic time.

An approximate scale of the absolute geologic time [J. P. Marble, 4] was compiled from the data obtained by the lead method for the radioactive and for the accessory minerals of magmatic origin. It is perfectly evident that estimations of the age of sedimentary rocks on he basis of their relationships to the intrusives is hindered by many obstacles on many occasions. For that reason, determinations of the age of post-Precambrian sediments directly from the sedimentary authigenic minerals contained therein, particularly from glauconites which are so abundant in sediments, both in space and in time, are pregnant with the possibilities of providing us with an absolute geochronologic scale, especially since the relative age of sedimentary bodies of different type may be confirmed by their characteristic lora and fauna.

The first attempts by the authors (1956), in determinations of the age of two glauconite specimens, proved to be a success and served as incentives for more systematic studies of glauconites in regard to heir age, within a wide range of geologic time, from the Sinian to the Neogene.

This work required collection of a great bulk of lithological material in the field. Some of these materials were collected personally by one of the authors, and some of them were procured from various geologic and industrial agencies of the Union and of the countries of People's Democracies. The authors take this opportunity to express heir thanks to all persons and organizations who participated in the selection of the reliably dated specimens of glauconite-bearing rocks and who placed specimens from exploratory boreholes at our disposal.*

A BRIEF MINERALOGICAL-LITHOLOGICAL DESCRIPTION OF GLAUCONITES

In relation to the studies of S. Hendricks and C. Ross [5], a unanimous opinion has been gained by mineralogists and petrographers, to he effect that glauconite is a potassium-iron silicate of the mica group. These authors, and also R. Grim [6], J. Gruner [7], K. mulikowski [8], M. F. Vikulova et al. [9], point out that glauconite is a dioctahedral illite (hydromica) in which Al^{3+} is largely replaced by Fe^{3+}, Fe^{2+}, and Mg^{2+} and in which as much as 2/3 of the possible ositions are replaced in such manner. Consequently, the tetrahedral nd the octahedral lattices of glauconite are negatively charged and

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Lithologic-mineralogic treatments of the test materials were conducted at the Laboratory of Geochemistry of Sedimentary Rocks (GEOKHI, AN SSSR); the age determinations were made at the Laboratory of the Absolute Age (VSEGEI).

these charges are balanced by cations (K^+, Na^+, Ca^{2+}) between the layers. Thus the composition of glauconite is variable, with potassium ranging from 1.5 to 8%. The general chemical formula of glauconite is as follows: $(K,Ca_{0.5},Na)_n(Al,Fe^{3+},Fe^{2+},Mg)_2(Si,Al,Fe^{3+})_4O_{10}(OH)_2 \cdot x H_2O$, where "n" is generally smaller than 1. Glauconite is formed almost exclusively in marine sediments during their diagenesis in seas at ordinary salinity and has a significant dependence upon sea currents.

Glauconite is weathered into clayey lumplets consisting of silicate-clay minerals, in the zone of ground water activity and on contact with atmospheric precipitates, according to L. N. Formozova [10]. It may be stated confidently even now that, beginning with the late Precambrian, there was scarcely a period in the history of the earth's evolution which would not be represented by some kind of glauconite-bearing sedimentary rocks.

Even in the concrete and specific example of the Russian Platform, glauconite is found in all sedimentary rocks of marine origin, from the Sinian to the Miocene.

We have no data on the presence of glauconite for the Triassic sediments of the Russian Platform, although there are such data on record for the Triassic sediments of Europe, America, and elsewhere, according to K. Hummel [11].

Glauconite is found chiefly in sandy-salty rocks, although it is also common in carbonate and clay rocks. Glauconite is especially abundant in the platform sediments and also in the marginal troughs; it is only rarely found in geosynclines, according to L. I. Gorbunova [12], L. N. Formozova [13], and E. K. Lazarenko [14].

In the vast majority of cases, glauconite is an authigenic mineral formed in the course of diagenesis and syngenetic with its host rock. Thus, the glauconite-forming stage is synchronous with the formation of the sedimentary rock itself, which is especially valuable in the geochronologic studies.

As previously stated, the weathering processes affect only those of the glauconite-bearing rocks that are within the zone of action of atmospheric and ground waters. L. N. Formozova [10] showed that there are significant changes in the chemical composition of glauconite only in specimens taken directly below the soil mantle and to depths not exceeding 1.3 meters below the surface of the sedimentary rock (depending on the depth of penetration by the atmospheric waters). There are no noticeable changes in alkalies below this depth, no changes in potassium, the element of special interest. The insignificant depths of weathering of glauconitic rocks were indicated also by A. V. Kazakov [15, 16], G. I. Bushinskii [17], and other authors.

Glauconites are weathered in successive stages. Glauconite turns somewhat brown at first and then brown-green, so that the parts of the mineral preserving their green color are most commonly in the cores of the grains; in the final stage, glauconite turns into brown pseudoolitic grains (resembling ferruginous oolites) which spread out, in the nd, into shapeless ferruginous spots on the rock.

The fairly high potassium content of glauconites, the wide distribuion of glauconites in sediments, their common syngenesis with sedinents, and the relative ease of visual appraisals of the state of their reservation, are the basic criteria that lead us to the belief that lauconite is a highly promising object for geochronologic studies.

SEPARATION OF GLAUCONITIC SEDIMENTARY ROCKS

Since glauconites are present in all fundamental lithologic types of edimentary rocks (sands, silts, clays and carbonates), there must be ertain appropriate modifications in the procedures for its separation rom the sediments. While undertaking the isolation of glauconite, reardless of the composition of the rock, we must first find out which articular size fraction contains most of it, prior to separation of the ingle-mineral (glauconitic) fraction.

Appraisals of the size of glauconitic grains are done under the nicroscope. If the rock is friable, its pelitic fraction is first elutrited with a small amount of water, and next the dry residue is examned under a binocular lens. We endeavored to obtain for the analysis he purest fraction of the mineral, free from admixtures of terrigenic naterials containing potassium that would cause large distortions in he determined age. This problem was solved successfully for pracically every rock specimen employed in the present study. The sepaation of glauconite was performed by the procedure outlined on page 78.

The procedure we employed made it possible to isolate the singleineral glauconitic fraction, practically in every case, with only 2 to % foreign minerals, chiefly quartz. In separating glauconite from arbonate rocks the material was fragmented to a particle size somehat coarser than the glauconite grains; the carbonate was dissolved n cold 3 to 5% HCl; after elutriation of the pelitic fraction and after rying of the residue the sample was subjected (if required) to electroagnetic separation.

Some difficult samples (up to 6 or 10 grams) had to be subjected to ielectric separation [E. V. Rozhkova, 18], by the means of aqueous ioxane (distilled water; 1:9 to 1:12) or, more rarely, by nitrobenzol ith kerosene. The change in the "d.p."* was from 5.2 to 6.2 on the verage.

Good yields of pure glauconitic fractions (up to 100 and 150 grams) ere obtained by the procedure here described.

'd.p.", in this connection, is obscure to the translator. VPS

Outline of Procedure for Separation of Glauconite from Sandy-Clayey Rocks

Operation No.	Sequence of operations	Basic prerequisites (in brief)
1	Fragmentation of rock to the particle-size glauconite	Done in procelain or iron mortar by vertical strokes of the pestle; rubbing would deform glauconite crystals; chopper grinder may be used, with 2 mm slit.
2	Screening through 0.1, 0.25, 0.5 mm sieves and collection of the desired fraction	Glauconite is found most commonly in the <0.1, 0.1, and 0.25 mm fractions
3	Elutriation by water, so as to remove the pelitic fraction, and drying at 60 to 70° C	Elutriation of clayey rocks is best on screens with openings 0.04 to 0.05 mm diam.
4	Examination of fractions under binocular lens	In order to ascertain absence of glauconitic clusters and mineralogic composition of the fractions.
5	Magnetic separation	Removal of magnetic minerals
6	Electromagnetic separation (repeated 2 to 3 times)	We use a single-pole wedge-shaped electromagnet, of Okunev's design, at 100 to 80 mv voltage which is fairly effective for grains of quartz, feldspar, and other non-electromagnetic minerals. The repeated separation is done at 60 mv, with the resulting concentrate consisting of 80 to 90% glauconite.
7	Purification from contaminants by heavy-liquid separation	The heavy fraction is isolated with the aid of bromoform or methylene iodide (sp. gr. 2.8 to 3.2); the heavy liquid is washed off and the mineral fraction is dried.
8	Picking out contaminating particles by a needle under the binocular	

DETERMINATION OF POTASSIUM AND ARGON IN GLAUCONITES

Potassium in glauconites was determined by the dipicrylamine method which is generally employed for its determination in silicates [G. A. Murina et al., 19]. Although the decomposition of glauconites was done by a mixture of hydrofluoric and sulfuric acids, the process

Table 1. The Absolute Age of Dated Glauconites

Item	Source	%K	10^{-7} g/g	Ar^{40}/K^{40}	Free argon,† % of total Ar	Age, million yrs	Geologic age	Remarks
1	Predkavkze'e; Umantzevo Borehole 59	5.31	0.135	0.0021	25	35	Pg_3^{KiV}	-
2	Kodor, Abkhaziya	6.99	0.254	0.0035	60	56	Pg_1^2	-
3	Czechoslovakia	4.42	0.363	0.0068	21	110	Cr_2^{cm}	Impure when isolated
4	Czechoslovakia	6.0	0.332	0.0043	10	70	Cr_2^{cm}	-
5	Predkavkaz'e*; Vyselki Borehole	4.41	0.384	0.0072	19	114	Cr_1^{alb}	-
6	N. Caucasus; Bolshaya Laba River	3.97	0.298	0.0058	26	95	Cr_1^{alb}	Hydromicas present
7	N. Caucasus; Bolshaya Laba River	5.72	0.414	0.0061	20	98	Cr_1^{apt}	-
8	Bukanskoe Deposit; Kaluga Area	5.78	0.317	0.0046	12	75	Cr_2^{cm}	Hydromicas present
9	Baksan River, Caucasus	5.0	0.372	0.0074	9	115	Cr_1^{art}	-
10	Ingur River, Georgia (Gruziya)	5.68	0.363	0.0053	15	85	Cr_1^{br}	-
11	Egor'evskoe Deposit; Moscow Area	5.23	0.503	0.0080	-	130	J_3vlg	-
12	The Mouth of Vyatka River	5.68	0.690	0.0101	15	160	P_2^{kz}	-
13	Varvarovskaya Borehole; Kuibyshev Area	5.24	0.955	0.015	12	230	C_2^{vr}	-
14	N. slope at Lebezhenki Village; Voronezh	6.78	1.68	0.0206	6	310	D_3^{Ivor}	-
5	Maardu Deposit, Estonia	6.65	2.38	0.0300	-	435	O_1	
	Maardu Deposit, Estonia		2.43	0.0303	12	440	O_1	-
	Maardu Deposit, Estonia		2.39	0.0295	9	430	O_1	-
6	Borehole R2, Kupa Village, BSSR (Belorussia)	5.35	1.87	0.0260	4	385	Cm_1'	-
7	Borehole R2, Kupa Village, BSSR (Belorussia)	5.83	3.00	0.0426	1.5	592	Cm_1	-
8	Lipyagi Village; Borehole R1	5.84	2.68	0.0382	7	540	Cm_1	-
9	Serdobskaya Borehole R2; 1380 m. depth	5.33	2.56	0.0402	37	560	Cm_1	-
0	Serdobskaya Borehole R2; 1787 m. depth	6.12	3.76	0.0515	3	690	Sn_2	-
	Serdobskaya Borehole R2; 1787 m. depth	6.12	3.70	0.0503	-	680	Sn_2	-
1	Serdobskaya Borehole R2; 1758 m. depth	4.90	2.95	0.0505	6	685	Sn_2	
2	Drillcore 18; Minyar Lake, Ural	5.90	5.43	0.0675	2	865	Sn	-

"Predkavkaz'e", "the fore-Caucasus", is the territory bordering on the great Caucasus in the north. VPS

That is, % of total argon in the sample; the rest of the argon is in the adsorbed state. In the original this column is headed "% A in air". VPS was accompanied by certain difficulties. The results in Table 1 show percentages of potassium in glauconites of about the same degree of purity. They show that the potassium content of glauconites is variable and that the range of its variation in our samples is from 3.97 to 6.99% i.e., nearly a two-fold variation.

There were appreciable difficulties in the determination of radiogenic argon in glauconites, and the common isolation procedure for argon (by warming and fusion of the mineral in vacuo) proved to be worthless.

Glauconites are generally present in rocks in a finely dispersed state (in the < 0.25 mm fraction). This makes it very inconvenient, even in the very first stage of the analysis, to collect the adsorbed gaseous argon in vacuo. Fine and light-weight particles of the mineral "fly" into the apparatus despite the most careful pumping. We found it possible to avoid this by inserting a quartz-wool plug into the quartz test tube containing the mineral. The plug was placed above the zone to which the heat was applied. Particles of glauconite intercepted by the plug were shaken down by a gentle tapping on the walls of the test tube.

The difficulties arising in the heating of glauconite were more serious. Glauconite contains appreciable quantities of both adsorbed and constitutional water which is separated from the mineral respectively at 100° and at 500°C [L. I. Tsvetkov and E. P. Valyashikhina, 20]. As the water vapor passes into the vacuum, it drags along some particles of glauconite to the walls of the quartz test tube considerably above the zone to which the heat is applied.

After several unsuccessful trials, we became convinced that the standard procedure is by no means a guarantee of satisfactory results. We gave it up, for that reason, and decided to heat glauconite not in vacuo but in the atmosphere of carbon dioxide. The pressure inside the quartz tube was maintained at about 0.75 to 1 atm. Depending on the heating of glauconite, and the corresponding increase in pressure, due to the liberated water vapor and other gases, the pressure inside the tube reduced to its original level by a partial freezing-out of water vapor and of carbon dioxide in a trap which was cooled by liquid oxygen. The pressure was controlled by a manometer and was equalized several times during the experiment, to the point of cessation of the escape of the water vapor, whereupon all of the carbon dioxide and the water vapor were frozen out in the trap and the subsequent purification of argon from chemically inert gases could be carried out by the common procedure [E. K. Gerling and T. G. Pavlova, 21; E. K. Gerling, M. L. Yashchenko, et al., 22]. Measurements of the isolated argon were made with the aid of the McLeod manometer and its isotopic composition was determined in the MS-2M mass spectrometer.

Heating glauconite in the CO_2 atmosphere assured the isolation of argon, without any fear that a part of the sample would be expelled with the water vapor, which made it much easier for us to conduct the periments. The determination of argon is made in the apparatus described by V. D. rintzson and N. I. Chernova [23], with the rticipation of V. D. Sprintzson. The iso- pic analysis of argon was made by A. V. attes.

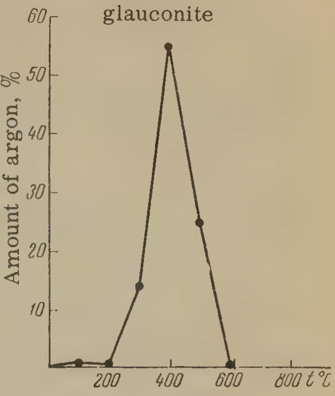

Fig. 1.

In order to learn of the character of sep- ation of argon from glauconite, in relation the temperature, we made an experiment volving measurements of the amounts of gon parted from glauconite at different mperatures. The experimental tempera- re range was from room temperature to 0°C, at 100°C-increments, and the evolu- on of argon was made complete at any ven and pre-determined tempera- re. The results of this experi- ent, conducted by G. A. Murina, e shown in Figure 1, where the scissa represents the tempera- re and the ordinate represents r cent argon separated from glau- nite at the indicated temperature s of total argon present in the sam- e). Figure 2 is a thermogram of uconite. It is evident from Fig- es 1 and 2 that the expulsion of the sorbed water (at about 100°C) does cause any liberation of argon; the latter begins at about 300°C. In actice, the complete liberation of argon takes place during dehydra- n of glauconite (500 to 650°C), i.e., during disruption of its crystal tice, and there is no further evolution of argon on further ignition.

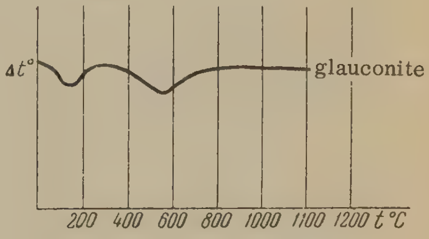

Fig. 2.

Consequently, in our determinations of argon, we did not try com- tely to fuse glauconite (at ca. 1250°C) and did not go over 800 to °C with the ignition.

The age was calculated with the aid of the following constants of radioactive decay of potassium: $\lambda_K = 6.02 \times 10^{-11}$ year^{-1}; $\lambda_\beta = 4.9 \times$ ^{10} year^{-1}.

RESULTS BY THE ARGON METHOD FOR DATED GLAUCONITES

We examined 22 samples of glauconite isolated from sedimentary ies with reliable biostratigraphic dating. Geographical orientation he samples, their exact position in the stratigraphic sections, and paleontologic premises of their dating are given below.

1. Glauconite from sandstone. Umantsevo Borehole No. 59, Pred- kaz'e. Upper Paleogene, Kiev Tier. 310 to 327 m. depth.

2. Glauconite from limestone with *Protocardium Edwardsi Desh, var. orientalis v.n., Spondylus sp., Area sp., Dentalium sp., etc.* Kodor River, Abkhaziya. Tops of the Lower Paleogene.

3. Glauconite from sandstone. Czechoslovakia, Melnik District, Koshatki settlement, Praga Area. Bottom of the Upper Cretaceous (Cenomanian).

4. Glauconite from sandstone. Czechoslovakia, Koberzhik Borehole, 76 to 77 m. horizon. Bottom of the Upper Cretaceous (Cenomanian).

5. Glauconite from clayey sandstones. Predkavkaz'e. The Vyselki orientation borehole. Lower Cretaceous (Upper Alb).

6. Glauconite from clayey aleurolites. Northern Caucasus, Bolshaya Laba River, Skryleeva Balka. Lower Cretaceous (Missle Alb).

7. Glauconite from clayey sandstones. Northern Caucasus, Bolshaya Laba River, Skryleeva Balka. Lower Cretaceous (Upper Apt).

8. Glauconite from sands. Bukanskoe Deposit, Kaluga Area. Upper Cretaceous (Cenomanian).

9. Glauconite from silts. Caucasus, Baksan River, Gundelen. Lower Cretaceous (Apt).

10. Glauconite from limestones. Georgia (Gruziya), Ingur River, Lower Cretaceous (Barrem).

11. Glauconite from clayey sands. Moscow Area, Egorevskoe Deposit; horizon under the phosphorites; *Oxynoticeras fulgens* fauna. Upper Jurassic (Volga Tier).

12. Glauconite from organogenic limestones. The mouth of Vyatka River, outcrop at Sokolki Village. Upper Permian (Kazan Tier).

13. Glauconite from silty marls. Kuibyshev Area, Varvarovskii Plot Borehole; 840.9 to 847.9 m. depth. Middle Carboniferous (Vereya Tier).

14. Glauconite from sandstones. Voronezh Massif, north of Novyi Oskol, Lezhenki Village; Borehole 38, 118.5 to 118.7 m. horizon. Upper Devonian (Voronezh Layers).

15. Glauconite from sandstones with *Orthis recta Paud. Megalaspis leuchtenbergi Lam. etc.* fauna. Estonian SSR, Maardu Deposit; Mine; Shaft 5.

16. Glauconite from limestones. Belorussian SSR, Kupa Station; Borehole R-2; 257 m. depth. Lower Cambrian.

17. Same as above; 2nd sample; 252 to 257 m. depth.

18. Glauconite from sandstones. Lipyagi Village, Borehole R-1; 1429.9 m. depth. Lower Cambrian, Valdai Complex, Lyaminarite Suite.

19. Glauconite from sandstones with relicts of pollen. *Palaeopirosaceus atavus Naum, Paleopirosaceus Poroscus Naum, Phosphosphaer*

laminarita Naum. The Serdobsk Orientation Borehole R-2; 1380 m. depth. Lower Cambrian, Valdai Complex, Lyaminarita Suite.

20. Glauconite from sandstones with relict pollen; *Brochosaccus antiqus Naum, Phosphosphaera notata Naum.* The Serdobsk Orientation Borehole R-2; 1787 m. depth. Upper Sinian, Inser Suite, Serdobsk Series.

21. Glauconite from sandstones. The Serdobsk Orientation Borehole R-2; 1758 m. depth. Upper Sinian, Inser Suite, Serdobsk Series.

22. Glauconite from sandstones. Ural, Minyar Lake; drillcore 18. Sinian, Inser Suite.

The age of glauconites here described varies within a wide range, from upper Paleogene to Sinian, and offering us the opportunity to test the argon method against these glauconites of such a markedly different age. The results are presented in Table 2.

The results in Table 2 show that radiogenic argon is preserved in glauconites for long periods of geologic time. The apparently too high age of Nos. 3, 5, and 9 is conspicuous. This should not be surprising, however, since they are the very samples that are the least pure because of the terrigenic hydromicas (Nos. 5 and 9) and feldspars (No. 3) that could not be eliminated in the separation of these glauconites. Supplementary test materials from these three sampling sites are now available, and particular care is to be given to their purification, so as to eliminate completely the admixtures interfering with the analyses.

The low age of glauconite No. 16, from the R-2 borehole, is somewhat surprising. The "rejuvenation" amounts to nearly two hundred million years, in this particular case. The characteristics of this sample are as follows: the glauconitic grains are of ordinary size 0.2 to 0.1 mm) but are noticeably bleached. During the isolation of the single-mineral fraction, the glauconitic grains vanished in the elutriation; they were apparently peptized and the glauconite passed into the most highly dispersed pelitic fraction. It is possible that some argon was lost in the process. Argon was much better preserved in the second sample from the same borehole and the corresponding age figure for the sample was entirely satisfactory.

As is evident from the table, the age results for glauconites in the same age-group (Lower Cretaceous, Cambrian, Sinian) are practically the same, within the ± 10% error of the analysis. The age results for the ancient glauconites are especially interesting because they are the first ones of the kind and because they demonstrate the possibility of the absolute dating of ancient sediments.

We attempted, in Table 2, a comparison of our results with all other available data on the absolute age of glauconites and with the approximate geologic timescale of T. P. Marble [4]. Because the American investigators do not use the same constant for the K-decay K^{40} as is now in use in the Soviet Union, we recalculated all our results and the results of Kh. I. Amirkhanov et al. on the basis of the

American constant $\lambda_K \pm 0.555 \times 10^{-10}$ year^{-1}* and of the λ_K/λ_β ratio of 0.117.

Columns 2 and 4, Table 2, contain the age data based on Gerling's constant and columns 3, 5, 6, 7—the age data based on the American constant. Column 9 shows the age limits of geologic periods by Marble's scale (his scale is based on the lead method).

Column 8 shows the age of glauconites as determined by R. Cormier, L. Herzog, W. Pinson, and P. Hurley [24] by the Sr^{87}/Rb^{87} method (the authors used the β-decay constant for rubidium, 1.38×10^{-11} year^{-1}, in their calculations of the age).

Table 2 shows a good agreement between the age of geologic formations, as determined by their

Table 2. The Absolute Age of Dated Glauconites by the Argon and the Strontium Methods

Geologic Age of Glauconites		Argon Method						Rubidium-Strontium Method; Cormier, Herzog, et al.	Approximate Scale of Geologic Time; Marble
		Our Data		Kh. I. Amirkhanov et al.		Wasserburg, Hayden, et al.; $\lambda^K/\lambda^\beta = 0.117$	Lipson; $\lambda^K/\lambda^\beta = 0.117$		
		$\lambda^K/\lambda^\beta = 0.125$	$\lambda^K/\lambda^\beta = 0.117$	$\lambda^K/\lambda^\beta = 0.125$	$K/\lambda^\beta = 0.117$				
Neogene	Miocene	-	-	20 to 25	22 to 27	-	18 to 32	-	12 to 28
Paleogene	Oligocene	-	-	30	33	-	14 to 22	-	28 to 40
	Eocene	35	38	40 to 60	43 to 64	48	34 to 35	60	40 to 60
	Paleocene	56	62	-	-	-	44	-	
Upper Cretaceous	Senonian	-	-	70 to 72	76 to 78	78	-	62 to 70	60 to 130
	Cognac	-	-	80	89		-		
	Cenomanian	70 to 110	76 to 120	-	-		-		
Lower Cretaceous	Albian	95 to 114	102 to 126	80 to 95	89 to 100	-	130	-	
	Aptian	98 to 115	81 to 127	90 to 130	100 to 139	-	-	-	
	Barrem	85	93	100	109	-	-	-	
Jurassic	Upper	130	139	135	145	-	-	-	130 to 160
Permian	Upper	160	175	-	-	-	-	-	185 to 220
Carboniferous	Upper	230	255	-	-	-	-	-	-
Devonian	Upper	310	340	-	-	-	-	-	265 to 320
Silurian	-	-	-	400	440	-	-	375 to 381	320 to 380
Ordovician	Lower	430 to 440	474 to 481	-	-	-	-	401 to 413	380 to 440
Cambrian	Upper	-	-	-	-	425	-	470	440 to 520
	Middle	-	-	-	-		-	-	
	Lower	540 to 560	600 to 620	-	-		-	-	520
Sinian	Upper	650 to 690	750 to 760	-	-	-	-	-	

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*In the Soviet Union, the age data obtained by the argon method are calculated on the basis of $\lambda_K = 0.602 \times 10^{-10}$ year $^{-1}$ which was determined experimentally by I. K. Gerling; the corresponding branching ratio = 0.125.

lauconites, and the approximate geologic time scale, notwithstanding
ertain departures in either direction. Beginning with the Devonian,
owever, and lower still, there is a tendency toward greater age for
he glauconites as against the age for the geologic time scale. Al-
hough the analyses here reported are not yet sufficient for a time
cale based on glauconites and a much larger body of reliable experi-
mental data is required for the purpose, the high promise of glaucon-
tes in the absolute dating of sedimentary geologic formations is
erfectly evident.

The authors realize that their work here reported is only the be-
inning of a far more difficult and painstaking endeavor, rewarding
evertheless: preparation of the absolute scale for the post-Pre-
ambrian geologic formations.

An extensive use of glauconites in the determinations of the age of
ediments may begin only after a whole series of methodical investi-
ations, particularly after an inquiry into the role of cation exchange
nd of sorption processes in the preservation of argon and potassium
n glauconites. It is not clear even now to what extent is the Ar/K
atio affected by the heavy liquids and the acid employed in the isola-
ion of the single-mineral fractions and to what extent this ratio may
e influenced by the degree of fragmentation of the sample. Only after
solution of these problems will it be possible for us to consider the
uitability of different kinds of glauconites for determinations of their
ge.

We may say with confidence even at this time, however, that the
tilization of glauconites as test materials in determinations of the
bsolute geologic age opens the possibilities of solution of some major
eologic problems with the aid of the argon method. These problems
re as follows:

1. Comparisons between the absolute age of sedimentary rocks
ith their relative geologic age, inasmuch as many sedimentary for-
mations are well dated biostratigraphically.

2. Correlations of ancient sediments that cannot be characterized
y their fauna over extensive areas.

3. Procurement of more reliable data on the duration of the evolu-
on of fossil forms of different kinds.

4. Appraisal of the rates of sedimentation in different tectonic
ones of the earth's crust.

5. Determination of the absolute age of some sedimentary ore de-
osits of iron, manganese, phosphate, and others.

6. The possibility of differentiation of the Upper Precambrian and
f narrowing the hiatus between the dated Lower Paleozoic and the
roterozoic (the hiatus is 520 to 1000 million years).

In such connections, we came to believe that work with the utiliza-
on of glauconites and of certain other authigenic minerals in the age
terminations by the argon method, together with special studies of
e preservation of radiogenic argon in glauconites, is absolutely

indispensable. A large number of glauconite specimens of different age is now at our disposal and the determinations of their age are being continued.

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REFERENCES

1. Wasserburg, G. J., R. J. Hayden, and K. J. Jensen. Ar^{40}/K^{40} dating of igneous rocks and sediments. *Geochim. et Cosmochim. Acta*, 10, No. 3, 153-166, 1956.
2. Lipson, J. I. K/A dating of sediments. *Geochim. et Cosmochim. Acta.*, 10, No. 1/2, 149, 1956.
3. Amirkhanov, K. I., K. S. Magataev, and S. B. Brandt. Opredelenie Absolyutnogo Vozrasta Osadochnykj Mineralov Radiologicheskimi Metodami (Determination of the absolute age of sedimentary minerals by radiation methods). *Doklady Akad. Nauk*, T. 117, No. 4, Geol. Ser., 1957.
4. Marble, J. P. The National Research Council (USA), Washington, 1950.
5. Hendricks, S. B., and C. S. Ross. The chemical composition and genesis of glauconite and celadonite. *Am. Mineral.*, 26, 1941.
6. Grim, R. E. Mineralogiya Glin (Mineralogy of Clays). Foreign Literature Press, Moscow, 1956.
7. Gruner, J. W. The structural relationship of glauconite and mica. *Am. Mineral.*, 20, No. 10, 1935.
8. Smulikowski, K. The problem of glauconite. *Archiv. mineral.* T. XVIII, *Zesz., Warszawa*, 1954.
9. Vikulova, M. F., B. B. Zvyagin, N. V. Iogansen, and V. I. Mikheev. Mineralogicheskoe Issledovanie Glavkonita iz Devonskikh Otlozhenii Voronezhskoi Oblasti (Mineralogic investigation of glauconite from Devonian sediments in Voronezh area). Mater. po Geol. Evrop. Chasti SSSR (Materials of geology of the European part of the USSR). *Gosgeolizdat*, 1952.
10. Formozova, L. N. K Voprosu o Vozraste Drevnei Kory Vyvetrivaniya na Yu. Urale (Age of the ancient weathered crust in Southern Ural). *Bull. Mosk. Ob-va Ispyt. Prirody*, Otd. Geol., T. XXII(2), 1947.
11. Hummel, K. Die Etenstehung eisenreicher Gesteine durch Halmyrolyse. *Geol. Rundschau.*, 13, No. 1, 1923.
12. Gorbunova, L. I. Glavkonity Yurskikh i Nizhnemelovykh Otlozhenii Tsentral'nykj Chastei Russkoi Platformy (Glauconites of Jurassic and Lower Cretaceous sediments in central parts of the Russian Platform). *Trudy in-ta Geol. Nauk*, Vyp. 114, Geol. Ser., No. 40, 1050.
13. Formozova, L. N. Glavkonitovye Peski Urochishcha* Kyzyl-Sai (Glauconitic sands of Kyzyl-Sai). *Trudy in-ta Geol. Nauk, Akad. Nauk SSSR*, Vyp. 112, Geol. Ser., No. 38, 1949.
14. Lazarenko, E. K. Problemy Nomenklatury i Klassifikatsii Glavkonita (Problems in taxonomy and classification of glauconites). Vop. Mineral. O sad. Obrazov (Problems in Mineralogy of Sedimentary Formations), kn. 3-4, izd. L'vovsk. Univ. (Books 3 and 4, Univ. of Lvov Press), 1956.

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*"Urochishche" is any natural landmark: a gulley, a tree, a rock; this term is left untranslated. VPS

Kazakov, A. V. Litologiya i Protesessy Vyvetrivaniya Fosfatnoi Kolonki Egor'evskoi Gruppy M-nii (Lithology and weathering processes in the phosphate section of the deposits of the Egor'evskaya group). *Trudy NIUIF*, Vyp. 140, 1938.

Kazakov, A. V. and E. N. Isakov. Glavkonit Egor'evskogo M-niya Fosforitov (Glauconite from the Egor'evskoe phosphate deposit). *Zap. Vseross. Mineral. Ob-va*, T. LXIX, No. 1, 1940.

Bushinskii, G. I. Petrografiya i Nekotorye Voprosy Genezisa Egor'evskikh Fosforitov Moskovskoi Oblasti (Petrography and certain problems in the origin of the Egor'evskoe phosphates of Moscow area). *Bull. Mosk. Ob-va Ispyt. Prirody*, Otd. Geolog., 15, 1937.

Sovremennye Metody Mineralogicheskogo Issledovaniya Gornykh Porod Rud i Mineralov (Modern Methods of Examinations of Rocks, Ores, and Minerals). Sborn. tr. VIMS (Coll. Papers, All-Union Inst. Mineral Raw Mater.) edited by E. V. Rozhkova, 1957.

Murina, G. A., A. D. Iskanderova, and V. D. Sprintzson. Sravnitel'naya Kharakteristika Analiticheskikh Metodov Opredeleniya Kaliya v Prilozhenii K Silikatam (Comparison of different analytical methods of determining potassium in silicates). Inform. sborn. Vses. n.-i. geol. in-ta (Coll. Inform. Papers, All-Union Inst. Geol. Res.) No. 3, 1956.

Tsvetkov, L. I., and E. P. Volyashikhina. Materialy po Termicheskomu Issledovaniyu Mineralov III Slyudy (Materials on thermographic studies of minerals in the mica III group). *Trudy in-ta geol. rudnykh m-nii. petrog. mineral. i geokhim.*, Vyp. 4, 1956.

Gerling, E. K., and T. G. Pavlova Opredelenie Geologicheskogo Vozrasta Dvukh Kamennykj Meteoritov po Argonovomu Metodu (Determination of the geologic age of two stony meteorites by the Argon Method). *Doklady Akad. Nauk SSSR*, T. 77, No. 1, 1951.

Gerling, E. K., M. L. Yashchenko, et al. Pervyi Opyt Primeneniya Argonovogo Metoda Opredeleniya Vozrasta Mineralov (The first experiment in determining the age of minerals by the Argon Method). *Doklady Akad. Nauk SSSR*, T. 86, No. 3, 1952.

Sprintzson, V. D., and N. N. Chernova. Sdvoennaya Argonovaya Ustanovka (The doubled-up Argon installation). *Inform. sborn. VESGEI*, No. 3, 1956.

Cormier, R. F., L. F. Herzog, W. H. Pinson, and P. M. Hurley. Rubidium-Strontium Age Determinations of the Mineral Glauconite. Massachusetts Inst. of Tech., Cambridge, 1957.

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THE ROLE OF COMPLEXES IN TRANSFERS AND ACCUMULATIONS OF RARE ELEMENTS IN ENDOGENIC SOLUTIONS

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Abstract

Under conditions of high concentration of strong bases and acids complex compounds are the most probable form of existence in aqueous and supercritical solutions for rare elements that are typical amphoteres (Be, Nb, Ta, Zr, Hf, etc.) or very weak bases (Sc, TR, etc.). In such solutions F, Cl, CO_3, PO_4, etc., may be added. The disintegration of rare-metal complexes and the formation of solid phases may be chiefly caused by two factors: 1) reaction of dissociated ions of the rare-element complex with solution components, 2) hydrolysis of the complex in the process of pH increase in the solution. On the basis of the law of mass action it has been shown that in these processes a regular separation even of elements with similar properties must occur, the complexes of which show different stability. At the same time elements differing by their chemical properties, the acidocomplexes of which show a similar stability, may precipitate into the solid phase practically simultaneously. The change of pH is considered as an important and continuously acting factor of rare-element concentration.

The behavior of rare elements with similar properties, the complexes of which are of different stability, is shown on examples of separating niobium and tantalum, rare earths of the cerium and yttrium groups etc., in the process of pegmatite formation. At the same time the closest paragenesis of Be, Nb and Zr in granite pegmatites of Nb and Zr in albitized alkaline and acid rocks etc. is considered from the point of view of similar stability of their complex compounds.

Forms of transfers of elements in post-magmatic solutions are among the most interesting problems in modern geochemistry. A solution of these problems would enable us not only to predict the characteristic behavior of the elements in question in geologic and geochemical environments of this kind, but also provide us with objective criteria for appraisals of the state and composition of mineral-forming solutions in different stages of the post-magmatic process.

The major role of complexes in transfers and deposition of chemical elements in the supergene zone was examined in detail by V. V. Shcherbina, using as examples certain chalcophile elements, gold, uranium, and titanium [9]. He also pointed out the probability of the participation of complexes in the transfers of a number of elements in the endogenic formation of minerals [10]. The latter observation is specially applicable to the majority of the rare elements, namely, to e typically amphoteric ones (Be, Zr, Hf, Nb, Ta, etc.) and to the very eak bases (Sc, rare earths, etc.) showing a measure of the capacity form complexes.

Complex compounds (“acidocomplexes”) are the most probable rms of these elements, both in aqueous and in super-critical solu- ons in the presence of high concentrations of strong bases and acids. epending on composition of the solutions, the addenda in such com- lexes may be fluorine, chlorine, CO_3, HCO_3, as well as other anions r anion groups, particularly the phosphates.

We must remark that the analysis of paragenetic associations of inerals in deposits of the rare elements in question, as well as the ata on gaseous-liquid inclusions in minerals of the rare metals and in e accessory minerals, with certain minor exceptions, permits us to egard the accumulations of the rare elements in the deposits as due the action of mineral-forming solutions enriched in the alkalies hiefly Na) and characterized also by their relatively high activity of tal acids (F^-, Cl^-, CO_3^{2-}, HCO_3^-).

Unfortunately, very little is known about complexes of the rare ele- ents. Their relatively high solubilities nevertheless enable us to rm the opinion that they are mobile substances capable of easy mi- ration [8, 11, 12]. It is also known that all of the rare metal com- lexes are stable only in certain narrow ranges of alkalinity of the lutions. This latter limitation is very important in the geochemistry the rare elements and is indeed responsible for the origin, migra- on, and decomposition of their complexes during the evolution of ineral-forming solutions.

It should be reasonable here to discuss certain propositions derived om the Mass Action Law, so as to clarify our concepts concerning e mobilities of the complexes of rare elements in the regularly volving acid-alkaline environments of mineral-forming solutions. As e know, the stability of a complex is generally defined by its “in- ability constant” (K_n) which is expressed conventionally by the quation $(M)(A)^n/(MA_n) = K_n$, where (MA_n) is the concentration of e complex ions in the solution, (M) is the concentration of the dis- ociated cations (in our case, Be, Ta, Nb, etc.), and $(A)^n$ is the con- ntration of the dissociated anions comprising the addendum.

Assuming invariability of the constant K_n, an increase in the con- ntration of the addendum ions in the solution will result in an in- ease in the stability of the complex, while depressing the concentra- on of the dissociated cations of the complex-forming metal. The ost favorable environment, therefore, for formation of rare metal mplexes in hydrothermal solutions is the environment with high con- ntrations of anionic addenda (F^-, Cl^-, CO_3^{2-}, HCO_3^-, etc.).

A lowering of the concentrations of the anionic addenda in the solu- on will lead conversely to a decomposition of the MA_n complex and a parallel increase in the concentration of the dissociated metallic cations (M). Also, a decrease in the concentration of the dissociated cations of the complex-former (M) will be conducive to a decomposition of the complex, provided $(A)^n$ remains constant.

Thus the decomposition of complexes of the rare elements during the evolution of mineral-forming solutions, upon which the possibility of a separation of the metallic complex-former into the solid phase depends, is determined mainly by the following two factors: a) A reaction between the dissociated ions of the rare element's "acido-complex" and some other constituent of the solution, resulting in the formation o an insoluble compound; b) Hydrolysis of the complex at increasing pH of the solution.

Formation of insoluble products by a reaction between certain constituents of the solution and the dissociated cations of the MA_n "acido-complex" is possible, if the concentration of the dissociated cations exceeds the critical level, which is dependent on the solubility-product (SP) of the sparingly soluble compound (mineral). Thus the possibility of a separation from the solution of this or that rare-metal mineral is determined by the concentration of the dissociated ions of the rare element in question, i.e., by the instability constant of its complex.

As an illustration, let us consider the simplest case involving a formation of a sparingly soluble phosphate of a trivalent cation M, as the result of a decomposition of the MA_n "acidocomplex":

$$MA_n + PO_4^{3-} \rightleftharpoons M^{n+} + nA^{1-} + PO_4^{3-} \rightleftharpoons MPO_4 + nA^{1-} .$$

The rate of the forward reaction, in the formation of the phosphate, equals: $V_{Fwd} = K_{Fwd} (M) \cdot (A)^n \cdot (PO_4)$, where K_{Fwd} is the rate constant of the forward reaction. If (PO_4) is constant, the rate of the reaction will depend entirely on the product $(M) \cdot (A)^n$, or, making use of the instability constant, on the product $K_n \cdot (MA_n)$.

Equilibrium for the given reaction occurs upon equalization of the rates of the forward and reverse reactions, $V_{Fwd} = V_{Rev}$, i.e., when $K_{Fwd} (M) \cdot (A)^n \cdot (PO_4) = K_{Rev} (MPO_4) \cdot (A)^n$.

However, the $(M) \cdot (PO_4)$ in the foregoing equation is the solubility product, SP_{MPO_4}, for the sparingly soluble phosphate MPO_4. In other words, equilibrium is determined entirely by the magnitude of SP_{MPO_4}. An increase in (M) causes an immediate shift of the equilibrium to the right and the consequent precipitation of MPO_4. From the relationship between the rate of the forward reaction and the instability constant, $V_{Fwd} = K_{Fwd} (M) \cdot (A)^n \cdot (PO_4) = K_{Fwd} \times K_n (MA_n) \cdot (PO_4)$, it follows that, in the presence of equal concentrations of the "acidocomplexes" of several elements in the solution yielding sparingly soluble compounds with any one of the solutes, there must be a precipitation of the element whose "acidocomplex" is characterized

the highest instability constant.* At the same time, the element
rming a stable complex characterized by the lowest instability con-
ant will remain in solution the longest.

Thus the ratio of the elements, M/Me, passing into the solid phase
any successive stage of the process is determined by the ratio of
e concentrations of their dissociated cations in the solution, (M)/(Me).
is latter ratio, in turn, depends on the instability constants and on
e concentrations of the acidocomplexes MA_n and MeA_n, i.e., is a
nction of the $K_{n_1}(MA_n)/K_{n_2}(MeA_n)$. In such a manner, during frac-
nal crystallization, there may be separations even of very similar
ements whose complexes differ from one another in their stabilities.

A very characteristic example of such fractionation is the passage
the rare earths into the solid phase in the process of formation of
anite pegmatites. It is evident from the studies of the sequence in
ich the rare earths minerals are formed in pegmatites that the
rium group passes into the solid phase (monazite, orthite) chiefly in
e relatively early stages of the pegmatitization, whereas the essen-
lly yttrium group minerals in pegmatites are generally crystallized
the late stages of the process.

In the presence of sufficient PO_4^{3-} in the melt, all of the rare earths
come fixed in monazite and xenotime, whereupon the over-all ratio
Y)/Σ(Ce) increases regularly during the process. E. Ingerson's
ta on distribution of the rare earths in two pegmatites from Minas
rais, Brazil, containing monazite and xenotime, are especially in-
resting [5]. These pegmatites, from their earliest to their latest
nes (in this particular case, from the "sahlbands" to the core of the
gmatitic body), show progressively increasing ratios of xenotime to
nazite as well as trends in the composition of the monazite itself,
expressed in the enrichment of the later varieties of this mineral
the less basic members of the rare earths group (Nd, Sm, Gd, Y)
d by thorium, as against the more basic La, Ce, and Pr.

This very definite enrichment of the residual fraction of the peg-
atitic melt-solution by the yttrium rare earths is explained by E.
gerson as being due to the greater stability of the complex compounds
rmed by the less basic rare earths of the yttrium sub-group and by
rium, as against the lesser stability of the complexes formed by the
rium sub-group. There is also a suggestion to the effect that the
latively mobile carbonate complexes of the rare earths may take
rt in the pegmatization.

Analogous results on the sequence of the rare earths separations
re obtained by A. P. Kalita [6] for the southwestern and the north-
stern Karelian pegmatites. The earliest rare-earths minerals in
ese pegmatites are represented by monazite and orthite, both of
m poor in the yttrium group, whereas the later stages of the

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ovided that the solubility products of all of the possible precipitates are ap-
oximately equal.

pegmatitic process are characterized by complex oxides of tantalum and niobium, of the types of euxenite, blomstrandite (probably betafite) and obruchevite (yttrian pyrochlore). A. P. Kalita presents convincing evidence of a genetic relationship between formation of the rare-earth minerals and the metasomatic phenomena taking place in the development of pegmatites. In this case, the fractionation of the rare earths, depending on their basicity, is even more complete than in the case described by E. Ingerson. In the case described by Kalita, the precipitation of the rare earths in the solid phase is not merely the result of a fixation of the dissociated cations by the anion PO_4^{3-} since the concentration of this anion proved to be adequate only for the fixation of a part of the cerium rare earths during the relatively early stages of the replacement. As a result, the yttrium rare earths are sorted, in these pegmatites, as complex oxide minerals, together with niobium, tantalum, titanium, uranium, during the later metasomatic stages, by the hydrolysis of their mobile complexes.

Taking into consideration the common tendency toward increasingly higher alkalinity of mineral-forming solutions in the course of the high-temperature metasomatic processes characteristic of accumulations of the rare elements, the relationship between the instability constant of the complex and variations in alkalinity of the solution becomes the subject of considerable interest in our explanation of the behavior of complex compounds in such environments.

As an example, let us consider the typical pattern of interaction between complex and hydroxide as exemplified by the reaction between sodium fluorberyllate and alkali:

$$2Na^+ + BeF_4^{2-} + 2OH^- \rightleftharpoons Be(OH)_2 + 4F^- + 2Na^+ .$$

The pH levels (7.5 to 8.0) at which the precipitation of beryllium hydroxide takes place, i.e., the transfer of beryllium to the solid phase were determined experimentally [7].

Discarding sodium from both sides of the equation, we may re-write the equation in its generalized form:

$$MA_n + mOH \rightleftharpoons M(OH)_m + nA^{1-}$$

From the Mass Action Law, the rates of the forward and the reverse reactions will be:

$$V_{Fwd} = K_{Fwd}(MA_n) \cdot (OH)^m ;$$

$$V_{Rev} = K_{Rev}(M(OH)_m) \cdot (A)^n ,$$

where K_{Fwd} and K_{Rev} are the rates of the forward and the reverse reactions respectively.

It follows from the equations that the rate of decomposition of the complex and the rate of formation of the sparingly soluble compound, $M(OH)_m$, increases markedly with increasing concentration of OH^-.

he rate of the reaction conducive to the formation of the MA_n comlex, on the contrary, depends significantly on the concentration of the cidic anion $(A)^n$. At chemical equilibrium,

$V_{Fwd} = V_{Rev}$ or $K_{Fwd}(MA_n) \cdot (OH)^m = K_{Rev}(M(OH)_m) \cdot (A)^n$;

ence:

$$(MA_n) = K_{Rev}/K_{Fwd} \cdot \frac{(A)^n \cdot (M(OH)_m)}{(OH)^m}$$

rom the equation:

$$K_n = \frac{(M) \cdot (A_1)^n}{(MA_n)} \; ; \; (MA_n) = \frac{(M) \cdot (A_1)^n}{K_n}^{*} .$$

y substitution:

$$K_n = \frac{K_{Fwd}}{K_{Rev}} \; \frac{(OH)^m \cdot (M) \cdot (A_1)^n}{(A)^n \cdot (M(OH)_m)} .$$

It follows from the equation so obtained that the stability of the mplex, in environments of varying alkalinity of the solution, is irectly proportional to the concentration of the ions of the addendum d inversely proportional to the concentration of OH^- and to the rate nstant for the hydrolysis of the complex. Relationships between ese magnitudes serve to determine accordingly the conditions under hich the rare-metal complexes are decomposed in mineral-forming lutions when their alkalinity is increasing progressively. The retionship between stability of the complex and the solubility of the oducts of its hydrolysis is also a factor of cardinal importance, asmuch as formation of insoluble products of the hydrolysis leads to rapid decomposition of the complex and to a rapid passage of the tire "M" quantity into the solid phase.

Thus variations in the pH which control hydrolysis of the rareetal complexes and the transfers of the rare metals into the solid ase, in environments with progressively increasing alkalinity of the ineral-forming solutions, constitute a major and a continuously erative variable in the accumulations of the rare metals into posits.

This latter factor is very clearly manifested in several deposits of e rare elements associated with replacement phenomena in which ere are accumulations of rare-metal minerals within the boundaries an advancing metasomatic front with its characteristically abrupt riations in alkalinity of the mineral-forming solutions. Such phemena are common in the case of beryllium, niobium, tantalum, and e rare earths in pegmatites as well as of beryllium in greisen posits [3], etc.

$_1$), as distinct from (A), is the concentration of the ions of the addendum dissociated as the result of the decomposition of MA_n in ordinary solutions.

The passage of the element into the solid phase should be determined in such circumstances entirely by the stability of its acidocomplex with respect to hydrolysis. As the result, depending on the increasing alkalinity of the solution, here too there may be a sorting of chemical elements whose chemical properties are very similar but whose acidocomplexes differ from each other in their stability. Concurrently, there may be a practically simultaneous passage into the solid phase of some chemically different elements whose acidocomplexes have about the same degree of stability. This thesis has an excellent illustration in the very close paragenesis between the early generation of beryl, columbite, and cyrtolite (Be, Nb, Zr) in granite pegmatites, of columbite and zircon (Nb, Zr) in albitized granite-porphyries, etc.

On the other hand, the well-known parting of such exceptionally similar, chemically, elements as niobium and tantalum or the cerium and the yttrium groups of the rare earths or, to some extent, of zirconium and hafnium, etc., in mineral-forming processes, may be explained most plausibly by differences in the properties of their complex compounds.

Thus complex compounds of tantalum and niobium possess different degrees of stability with respect to hydrolysis, whereas the differences between their solubilities are barely perceptible. Specifically the characteristic difference between the fluorides of these metals lies in the nearly quantitative decomposition of NbF_5 by solutions of alkalies, whereas TaF_5 yields oxyfluortantalates under the same conditions [8]. This behavior may account, to some extent, for the separation of niobium and tantalum in the granite-pegmatitic process, in consequenc of increasing alkalinity of the mineral-forming solutions during the progress of the sodium metasomatism (albitization). It should be adde that the procedure for separating these two very similar elements in practice is based on the unlike solubilities of potassium fluorniobate and fluortantalate.

The noticeable differences in both stability and solubility of the acidocomplexes of zirconium and of the more basic hafnium may be the real cause of the observed increase in the Zr/Hf ratio in zircons from albitized pegmatites and from some metasomatic deposits belonging to late stages of the process. As we know, fluorhafnium complexes are somewhat less stable than their fluorzirconium analogs and their solubilities are also not quite the same. The only practical method of separating zirconium from hafnium is based on the solubility differenc between K_2ZrF_6 and K_2KfF_6.

Differences in the stabilities of various complexes of the rare earths have already been discussed. Carbonate complexes of the rare earths, whose stability in water increases from $(La(CO_3))^{3-}$ to $(Lu(CO_3))^{3-}$, are the best known ones in this respect. This is in agreement with the opinion of E. Ingerson [5] who explains the accumulations of the least basic lanthanides and yttrium during the late stages

pegmatization by the greater stability of their complexes, as against
e complexes of the more basic members of the group.

Presupposing the possibility of transfer of rare metals in the form
complex compounds in solutions, we must take into consideration the
multaneous presence of different acidic anions in such solutions dur-
g the mineral-forming stages here visualized, with the implication
at such anions may play the role of the addenda. Under these condi-
ɔns, we may assume simultaneous presence of several acidocom-
exes of one and the same element in the mineral-forming solutions.
ıus F^-, Cl^-, HCO_3^-, CO_3^{2-}, and CO_2 are present invariably in the
.seous-liquid inclusions of beryl crystals belonging to different gen-
ations, as shown by analyses. Moreover, carbonic acid is enriched
inclusions in the youngest beryl of pegmatites (crystals in vugs), as
ell as in beryl (emerald) from low-temperature carbonate veins [2].
ı the other hand, beryls of the older generations (in pegmatites) are
aracterized by inclusions in the form of crystals of alkali fluorides
.d chlorides [4]. Taking into account the fact that such variations in
e composition of the gaseous-liquid inclusions in beryls of different
nerations may be observed in one and the same pegmatitic body, we
e justified in the assumption that the role of beryllium halide com-
exes decreases progressively whereas the role of beryllium carbon-
es increases progressively in the solution during the pegmatitic
ocess.* This conclusion seems to be at odds with what is known con-
rning the stability of beryllium complexes, among which the fluor-
ryllate is the most stable one (particularly in comparison with the
rbonate complexes of Be). However, we are led to assume a rela-
ely rapid decomposition of the fluorberyllate complex during the
rly stages of the process, despite its relatively high stability, if we
e into account the high activity of fluoride ion in reactions between
orine-bearing solutions and the wall rocks or the minerals belonging
earlier paragenetic complexes. A phenomenon of this sort should be
ecially characteristic of berylliferous pegmatites whose mineral-
ming solutions were not distinguished by their high content of
orine [2]. The author of this report has previously expressed the
nion that differences in the stabilities of complex compounds of
yllium in mineral-forming solutions are among the principal causes
the prolonged participation of beryllium in mineral-forming proc-
es and for its presence in several generations of minerals [1, 2].
ilar conclusions may be drawn with reference to tantalum and nio-
m in granite pegmatites, to zirconium in granite and syenite peg-
tites, etc.

In such a manner, concepts entailing the possibility of transfers of
e elements in the forms of complexes in endogenic solutions enable
on the assumption of certain concrete chemical relationships, to

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author regards the gaseous-liquid inclusions in minerals of the rare met-
as relicts of liquid and gaseous products of the decomposition of mobile
ıpounds of these metals in the course of crystallization of the mineral [4].

explain many of the formerly obscure characteristics of the distributio of these elements in post-magmatic deposits.

Success in further research on these problems is contingent on experimental studies on the behavior of the complex compounds of rare elements at high temperatures and pressures, as well as on the accumulation of experimental data on the composition of gaseous-liquid inclusions in minerals of rare metals.

REFERENCES

1. Beus, A. A. Geokhimiya Berilliya (Geochemistry of beryllium). Geokhimiya, No. 5, 1956.
2. Beus, A. A. K Geokhimii Berilliya v Granitnykh Pegmatitakh (Geochemistry of beryllium in granite pegmatites). *Izv. Akad. Nauk SSSR,* Ser. Geol. No. 8, 1957.
3. Beus, A. A. K Geokhimii Berilliya v Gidrotermal'no-Pnevmatolitichskom Protsesse (Geochemistry of beryllium in the pneumatolytic-hydrothermal process). *Trudy IMGRE, Akad. Nauk SSSR,* Vyp. 2, 1958.
4. Beus, A. A. and N. E. Zalashkova. O Genezise Natrievoi Raznovidnosti Berilla v Granitnykh Pegmatitakh (Origin of the sodium variety of beryl in granite pegmatites). *Mineral Sb. L'vovsk Geol. Ob-va pri Un-te* (Collected Papers in Mineralogy, Geol. Soc. Lvov), No. 10, 1956
5. Ingerson, E. Sostav Redkikh Zemel' v Monatsitakh iz dvukh Pegmatitov Brazilii (Composition of the rare earths in monazites from two Brazilian pegmatites). *Trudy Simp. po Geokhim. Redkikh Elementov v Izverzhennykh Gornykh Porodakh* (Proc. Symp. on Geochem. of Rare Elements in Igneous Rocks), 1958 (in press).
6. Kalita, A. P. Osobennosti Paragenezisa Aktsessornykh Redkometal'nykj Mineralov Pegmatitovoi Zhily Alakurtti No. 1 (Characteristics of paragenesis of rare metal accessory minerals of pegmatitic vein Alakurtti No. 1). *Trudy IMGRE, Akad. Nauk SSSR,* Vyp. 2, 1958 (in press).
7. Novoselova, A. N. Ob Osazhdenii Okisei Zheleza i Berilliya iz Ftoristykh Soedinenii (Precipitation of iron and beryllium oxides from compounds of fluorine). *Zhurn. Opy. Khim.,* T. 16, 1946.
8. Ryss, I. G. Khimiya Ftora i Ego Neorganicheskikh Soedinenii (Chemistry of fluorine and of its inorganic compounds). *Goskhimizdat,* 1956.
9. Shcherbina, V. V. Kompleksnye Soedineniya i Perenos Khimicheskikh Elementov v Zone Gipergeneza (Complex compounds in relation to transfers of chemical elements in the zone of supergenesis). *Geokhimiya,* No. 5, 1956.
10. Shcherbina, V. V. Formy Perenosa Khimicheskikh Elementov v Protsessak Mineralobrazovaniya i Usloviya Ikh Kontsentratsii (Forms of transfers of chemical elements in mineral-forming processes and factors conducive to their accumulation). *Vop. Geokh. i Mineral., Izd Akad. Nauk SSSR,* 1956.
11. Yatsimirskii, K. B. Ustoichivost' Kompleksynkh Soedinenii v Vodnykh Rastvorakh (Stability of complex compounds in aqueous solutions). *Uspekhi Khimii* 22, 4, 410, 1953.

2. Yatsimirskii, K. B. Termodinamika Rektsii Kompleksoobrazovaniya v Rastvorakh (Thermodynamics of complex-forming reactions in solutions). *Zh. Neorg. Khimii* (Journ. Inorganic Chem.), 11, Vyp. 3, 1957.

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THE COMPOSITION CHARACTERISTICS OF THE RARE EARTHS IN MINERALS*

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Abstract

The composition of rare earths is shown by two similar curves linking the points of separate even and odd lanthanides. According to the value of the maxi mum, three types of rare-earth composition have been distinguished: a strongl selective (> 45-50), a selective (> 30) and a complex type (< 30). Besides the well-known maxima on Ce, Dy and Yb, abrupt maxima of lanthanides in minera has been outlined. A correlative bond between near-lanthanides and a relative constancy in the ratios of even and odd elements of one pair has been establishe The correlative bond of the separate lanthanides depends on the proximity of th ionic radius (and electronic configuration) of one pair of elements. The typical ratios of pair lanthanides are somewhat disturbed in strongly selective compos tions. In minerals with maxima on Ce, Nd and Gd, Y is nearly absent, whereas in compositions with maxima of Dy and Yb, large amounts of Y are present.

Therefore in the mineralogical-geochemical respect it has been suggested t place the boundary between the cerium and yttrium groups between Tb and Dy. It is reasonable to distinguish the pair-lanthanide groups according to the leading even elements; the cerium group (Ce, La), the neodymium group (Nd, Pr), the samarium group (Sm, Eu), the gadolinium group (Gd, Tb), the dysprosium group (Dy, Ho), the erbium group (Er, Tu) and the ytterbium group (Yb, Lu).

Systematic studies of the rare earths in minerals were begun in th 1920's by V. M. Goldschmidt and L. Thomassen [1]. Although their studies were chiefly qualitative, they were sufficient to demonstrate that the rare earth minerals differ significantly among themselves in the proportions of the rare earths they contain.

Goldschmidt and Thomassen were able to differentiate several type of rare earth minerals on the basis of their composition and the relative preponderance of this or that element: a) the complex type (apati yttrium fluorite); b) the selectively cerium type (monazite, allanite); c) the selectively yttrium type (thalenite, thortveitite, xenotime).

Complete quantitative data on the composition of the rare-earth minerals have appeared in abundance chiefly in recent years, in the studies by I. B. Borovskii and V. I. Gerasimovskii [2], Murata et al. [4], E. E. Vainshtein, A. I. Tugarinov, and N. V. Turanskaya [5], and others [6, 7, 8, 9].

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We conducted systematic studies of the composition of the rare arths represented by more than 100 specimens of different minerals f different genetic types from different localities. Inasmuch as the arlier studies [2, 3, 4, 5] report quantitative characteristics of the are earths chiefly in cerium minerals, the present study was intended put a particular emphasis on yttrium minerals.

The mineral specimens were collected by E. I. Semenov during his udies in the Kola Peninsula, Ukraine, Urals, Central Asia, Taimyr, enisei Range, and Kolyma. Several specimens were procured from her geologists in the Union whose names are given in the analytical bles. The rare-earth minerals from foreign sources were procured om the collections of the Mineralogical Museum, Academy of ciences of the USSR, through the courtesy of G. P. Barsanov. The inerals were identified, in controversial cases, by X-ray and optical ethods.

Preliminary isolation of precipitates of the sum-total of the rare arths (ΣTR_2O_3) were performed for most of the minerals by A. V. ykova, O. F. Dorondova, M. E. Kazakova, M. V. Kukharchik, and I. S. azina, chemist-analysts. The quantitative composition of the rare rths in the ΣTR_2O_3 or in the minerals was determined by R. L. arinskii by the X-ray spectrographic procedure. Reliability of the alyses was 5 to 7% of the determined values, with a sensitivity of 1%.

Results of the X-ray spectrographic analyses are presented in the ble. Figures in the columns of the table indicate percentages of the ven lanthanide in the ΣTR_2O_3, which is here taken as 100%. All of e oxides are sesquioxides, with the exception of the oxides of Ce and which are assumed to be dioxides, by analogy with earlier reports , 4]. The point here is that Ce and Pr are present as dioxides in e working standards employed in the X-ray spectrographic analyses. should be possible to treat them as sesquioxides, for the sake of iformity of results.

Inasmuch as the rare-earth content of the minerals is generally ver than it is in the ΣTR_2O_3, the lanthanides are determined with gher sensitivity and with greater accuracy in the precipitate than in minerals. For that reason, whenever rare earths were determined ectly in minerals, the results are qualified in the table, by the word ineral'' in the footnote. Yttrium was determined by difference, 0% minus ΣTR_2O_3, in the minerals here examined. Consequently, results for yttrium are not quite as accurate as the results for the thanides.

Because the composition of the rare earths has been ascertained so only for very few minerals, it appeared desirable to include the er analyses together with the newer data for the same minerals. minerals which were already analyzed by the earlier investigators etail (tens and hundreds of specimens of monazite, allanite, etc.) report only the range of the variation for their composition.

Table 1. Composition of Rare Earths in Minerals ($\Sigma\,TR_2O_3 = 100\%$)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
1	Bastnaesite; $CeFCO_3$	Gallinas, N.M., USA; granite hydrotherm; extreme of 6 lanthanides	42.9	45.6	3.9	7.1	0.5	-	-	-	-	-	-	-	-	-	a)
2	Bastnaesite; $CeFCO_3$	Mountain Pass, Calif., USA; alkaline syenite hydrotherm; extreme of 6 high-Nd specimens	26.1	50.5	4.9	15.9	1.8	-	0.9	-	-	-	-	-	-	-	a)
3	Bastnaesite; $CeFCO_3$	Mochalin Log, Ural; alkali granite pegmatite	39	50	3.1	7.7	0.2	-	-	-	-	-	-	-	-	-	a)
4	Bastnaesite; $CeFCO_3$	Madagascar; granite pegmatite	34	53	3.8	8.5	0.7	-	0.1	-	-	-	-	-	-	-	b)
5	Bastnaesite; $CeFCO_3$	Tuva; hydrotherm of alkali granites	25	50	5.6	18	0.9	-	0.5	-	-	-	-	-	-	-	
6	Fluocerite; CeF_3	N. Kirgiziya; hydrotherm of granites	38	48.4	3.3	9.3	1.2	-	-	-	-	-	-	-	-	-	c)
7	Nordite; $Na_3Ce\,(Sr,Ca)\cdot(Mn,Fe)\,Si_6O_{17}$	Lovozero, Kola Peninsula; sodalite syenite pegmatite	34	55	4.1	7	-	-	-	-	-	-	-	-	-	-	
8	Ancylite; $Ce_4Sr_3(CO_3)_7\cdot(OH)_4\,H_2O$	Khibiny, Kola Peninsula; nepheline syenite; hydrothermal stage	32	54	4.1	9.5	0.3	-	-	-	-	-	-	-	-	-	
9	Parisite; $Ce_2Ca\,(CO_3)_3\,F_2$	Mountain Pass, Calif., USA; hydrotherm of alkali syenites	29.9	50.5	4.3	14	1.3	-	-	-	-	-	-	-	-	-	a)
10	Parisite; $Ce_2Ca\,(CO_3)_3\,F_2$	Mariupol, Ukraine; hydrotherm of alkali syenites	29.1	51	3.8	14.6	1.5	-	-	-	-	-	-	-	-	-	d)
11	Sahamalite; $Ce_2(Mg,Fe)\,(CO_3)_4$	Mountain Pass, Calif., USA; hydrotherm of alkali syenites	30	53	4	12	1	-	-	-	-	-	-	-	-	-	
12	Burbankite; $(Ce,Na,Ca,Sr,Ba)\,CO_3$	Bear Paw Mtn., Montana, USA; hydrotherm of alkali rocks	25.8	53.6	4.2	15.4	1.1	-	0.8	-	-	-	-	-	-	-	
13	Calkinsite; $Ce_2\,(CO_3)_3\cdot 4H_2O$	Bear Paw Mtn., Montana, USA; supergene after burbankite	30.7	52	4.5	12.3	-	-	-	-	-	-	-	-	-	-	
14	Florencite; $CeAl_3\,(PO_4)_2\cdot(OH)_6$	Ural diamond placers	29.2	48.6	5.4	16.8	-	-	-	-	-	-	-	-	-	-	
15	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Khibiny; neph. syenite pegmatite; hydrothermal stage	33	53	4.5	9	0.5	-	-	-	-	-	-	-	-	-	
16	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Ijolites; Kola Peninsula	24	54	6	15	0.7	0.3	-	-	-	-	-	-	-	-	
17	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Ijolites; Yenisei Range; Kiya	25	55	5.8	14	0.2	-	-	-	-	-	-	-	-	-	e)
18	Steenstrupine Na MnCe (Si	Lovozero; sodalite syenite pegmatite	24	48	7.3	20	0.7	-	-	-	-	-	-	-	-	-	

No.	Mineral and formula	Source and geologic features	La	Ce	Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
19	Cordylite; $Ce_2\ Ba\ (CO_3)_3F_2$	S.Greenland, Narsarsuk; alkali syenite pegmatite; hydrothermal stage	29	45	5.5	15	3.2	0.1	2.1	-	-	-	-	-	-	-	c)
20	Chevkinite; $Ce_1FE_2Ti_3Si_4O_{22}$	Vishnevye Gory; alkaline syenite pegmatite	34	51	3.8	11	0.2	-	-	-	-	-	-	-	-	-	f)
21	Chevkinite; $Ce_1Fe_2Ti_3Si_4O_{22}$	Keivy, Kola Peninsula; alkali syenite pegmatite	20.2	42.6	5.5	21.3	4.9	-	3.2	-	2.3	-	-	-	-	-	d)
22	Belovite; $Na_2Ce_2Sr_6\ P_6O_{21}\ (OH)_2$	Lovozero, alkali syenite pegmatite	22	52	7.8	18	0.5	-	-	-	-	-	-	-	-	-	
23	Rhabdophane $CePO_4 \cdot H_2O$	Ditto, hydrothermal stage	39	48	3.4	9.3	0.3	-	-	-	-	-	-	-	-	-	
24	Rhabdophane $CePO_4 \cdot H_2O$	Julianehaab, S. Greenland; alkali syenite pegmatite, supergene stage	35	56	3	6	-	-	-	-	-	-	-	-	-	-	c)
25	Rhabdophane $CePO_4 \cdot H_2O$	Sumy, Ukraine; sedimentary rocks	18.0	46	8	20	3.4	0.3	2	0.3	1.3	0.2	0.5	-	0.2	-	g)
26	Rinkolite $Na_2Ca_4Ce\ Ti\ Si_4\ O_{15}F_3$	Khibiny; nepheline syenite pegmatite; the La extremes of 12 analyses	27.6	45.6	4.9	16.3	2.6	-	1.6	-	1.4	-	-	-	-	-	h)
27	Rinkolite $Na_2Ca_4Ce\ Ti\ Si_1\ O_{15}F_3$	Ditto; the Nd extreme of 12 analyses	15	44.2	4.8	24.2	4.3	-	2.8	0.1	2.3	0.2	0.3	-	1.9	-	h)
28	Rinkolite $Na_2Ca_4Ce\ Ti\ Si_4\ O_{15}F_3$	Lovozero; nepheline syenite pegmatite	17	51	8	19	4	0.2	0.5	-	0.4	-	0.1	-	-	-	
29	Monazite, $CePO_4$	Kounrad, Kazakhstan; granite pegmatite; the La extreme of 100 specimens	37.7	49.3	3.1	9.0	0.9	-	-	-	-	-	-	-	-	-	i)
30	Monazite, $CePO_4$	Jamestown, Colo., USA; granite pegmatite; the Nd extreme of 100 specimens	13.1	41.5	6.1	32.9	4.4	-	2	-	-	-	-	-	-	-	
31	Monazite, $CePO_4$	Tommot, Yakutiya; alk. granite pegmatite	26	49	5.5	18	1	0.1	0.6	-	-	-	-	-	-	-	
32	Monazite, $CePO_4$	Borshchevochnyi Range, Transbaikal (pptd. cerium group)	20	51	7.4	18	1.8	0.1	1	-	0.3	-	0.3	-	0.2	-	
33	Monazite; $CePO_4$	Ditto (pptd yttrium group)	1.9	3.8	1	5	8	0.7	43	5.8	17	3.3	6	1	3	0.7	
34	Cerite; $Ce_2Si_2\ O_7 \cdot H_2O$	Mtn. Pass, Calif., USA; hydrotherm of Alkali Syenites (the La extreme of 4 specimens)	24	49.3	5.6	18.5	1.6	-	-	-	-	-	-	-	-	-	a)
35	Cerite; $Ce_2Si_2\ O_7 \cdot H_2O$	Jamestown, Colo., USA; granite pegmatite; (the Nd extreme of 4 specimens)	11	42.9	6.3	33.6	4.7	-	1.5	-	-	-	-	-	-	-	a)
36	Cerite; $Ce_2Si_2\ O_7 \cdot H_2O$	Bastnaes, Sweden; skarns	31	45	5.8	16	1.1	-	0.7	-	0.3	-	-	-	-	-	

Table 1. Composition of Rare Earths in Minerals ($\Sigma TR_2O_3 = 100\%$) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
37	Gorceixite; $BaAl_3(PO_4)(HPO_4)(OH)_6$	Minas Gerais, Brazil; diamond placers	17.5	39.1	6.3	26.6	6.4	-	4.1	-	-	-	-	-	-	-	a)
38	Knopite; $Ca(Ti, Fe, Nb) O_3$	Kola Peninsula; alkaline pyroxenites	23	45	5.3	22	1.8	0.1	1.3	0.2	0.4	-	0.2	-	0.5	-	
39	Knopite; $Ca(Ti, Fe, Nb) O_3$	Taimyr: alkaline pyroxenites	19	51	7.2	19	1.8	0.1	1.1	0.2	0.4	0.2	0.2	-	-	-	
40	Knopite; $Ca(Ti, Fe, Nb) O_3$	Yakutiya; carbonatites	16	47	9.5	25	2	0.2	0.4	-	0.2	0.2	-	-	-	-	
41	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	USA; granite pegmatite	0.6	1.2	0.7	25	15	0.6	53	6	15	1.7	1.8	0.7	1	0.4	
42	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Shumilovka Mine, Transbaikal: granite pegmatite	0.6	2.1	1.3	6.6	22	0.6	29	5.6	20	2.5	4.1	1	3.5	0.8	
43	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Baits-Kundui, Transbaikal; granite pegmatite	1.3	3.5	1.7	7	15	1.2	24	3.6	15	3.4	8	1.6	12	2.4	
44	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Madagascar; granite pegmatite	0.6	1.8	1.5	4.7	14	0.5	23	4	20	2.7	11	1.9	12	2.1	
45	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Ilemeny, Ural; granite pegmatite	1	3.3	1	3.9	19	1	18	2.6	28	6.8	4.8	1	7.8	1.7	
46	Euxenite; $YNbTiO_6$	Romteland, Norway; granite pegmatite	1.1	3	1.7	5.4	4.1	0.3	6.8	1.5	14	3.4	16	2.8	33	7	
47	Euxenite; $YNbTiO_6$	Kragero, Norway: granite pegmatite	5	16	2	6	1	-	7	1.5	14	3	8	1.4	30	5.3	b)
48	Euxenite: $YNbTiO_6$	Eliseevka, Ukraine; granite pegmatite	1.9	4	0.5	1.9	9	0.5	12	2	16	3.8	11	1.9	30	5	m)
49	Euxenite; $YNbTiO_6$	Romteland, Norway; granite pegmatite	0.5	1.3	0.2	0.5	5.8	0.5	14	2.6	18	3.8	16	2.9	29	4.9	-
50	Euxenite; $YNbTiO_6$	Iveland, Norway; granite pegmatite	1	3.7	1.2	3.5	5.7	0.5	11	2.4	17	4	13	2.3	29	5.6	-
51	Euxenite; $YNbTiO_6$	Iveland, Norway; granite pegmatite	3.7	13	1	3	4	0.2	9.2	2.2	13	3	12	1.8	29	5	b)
52	Euxenite; $YNbTiO_6$	Iveland, Norway: granite pegmatite	0.8	2.5	0.9	1.9	6.7	0.2	14	2.7	18	3.7	16	2.8	25	4.6	-
53	Euxenite; $YNbTiO_6$	Korovikha, Altai; granite	1.5	4.2	1.4	4.2	5	0.5	10	1.6	19	4.8	16	3	25	4.1	b)
54	Euxenite; $YNbTiO_6$	Adun-Chilon, Transbaikal; granite pegmatite	2.5	7.4	2.7	6	11	0.7	8	2.2	16	3.7	12	2.5	21	4.4	n)
55	Euxenite; $YNbTiO_6$	Arve, Norway; granite pegmatite	1.1	3.4	1.1	3.4	7.3	0.4	17	3	22	4.5	14	3	17	3	-
56	Euxenite: $YNbTiO_6$	N. Tuva; albitite of nepheline syenites	0.6	1.2	0.4	1.2	4	0.4	8	2.5	31	7.6	20	3.1	17	3.3	o)
57	Euxenite; $YNbTiO_6$	Hitterö, Norway; granite pegmatite	2	5	1.5	4.7	11	0.9	20	3.6	22	4.5	10	2	11	2	p)
58	Xenotime; YPO_4	Arendal, Norway; granite pegmatite; (the extreme of 11 specimens of Yb type)	-	-	-	-	-	-	13.2	-	2.4	-	21.4	5.4	46	11.6	i)

							8	9	10	11	12	13	14	15	16	17	18
Item No.	Mineral and formula	Source and geologic features	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Remarks
59	Xenotime; YPO_4	St.Gotthard, Switzerland; Alpine vein (the extreme of 11 specimens of Dy type)	-	-	-	-	2.9	-	14	3	36	7	18.6	-	15.8	2.9	i)
60	Xenotime; YPO_4	Omsukchan, Magadan District; hydrotherm of granites	-	-	-	-	3.8	-	13	3.5	28	6.7	22.6	-	18.9	3.5	d)
61	Xenotime; YPO_4	Placer, Ural	1.8	6	0.5	1.5	3.7	0.4	15	2.6	20	4.8	18	2.6	20	3	b)
62	Churchite; $YPO_4 \cdot 2H_2O$	Kiya, Krasnoyarsk Krai; alkali syenites, supergene stage	2.5	6.8	1.2	4.6	4	0.6	13	21	23	5.7	17	3	14	2.5	q)
63	Yttrialite; $(Y,Th)_2Si_2O_7$	N.Yakutiya; alkali granite pegmatite	2	7	2	7	6	0.2	10	2	20	4.1	15	2.2	19	3.2	r)
64	Thalenite; $Y_2Si_2O_7$	Upsala, Sweden; granite pegmatite	0.8	2.6	0.7	1.6	1.4	0.3	20	3.2	17	3.9	12	2	19	3.4	-
65	Fergusonite; $Y(Nb,Ta)O_4$	Iveland, Norway; granite pegmatite	0.5	2	1.4	4.3	5.1	0.2	7	1.4	9	2.2	8	2	48	9	-
66	Fergusonite; $Y(Nb,Ta)O_4$	Gierrestad, Norway; granite pegmatite	1.6	4	0.8	2.4	3.5	0.9	9	1.6	18	3.8	20	3.7	26	5	-
67	Fergusonite; $Y(Nb,Ta)O_4$	Ytterby, Sweden; granite pegmatite	1.6	6	0.3	1	2	0.1	8	2	13	3.4	16	2.6	38	6	b)
68	Fergusonite; $Y(Nb,Ta)O_4$	Kuramin Range, Central Asia; granite	3.3	11	2.6	8	8	0.5	11	2.2	10	2.6	11	1.7	24	4.2	s)
69	Fergusonite; $Y(Nb,Ta)O_4$	Evje, Norway; granite pegmatite	0.4	1	0.2	0.5	1.4	0.4	8.6	1.7	19	4.9	22	4	30	5.6	-
70	Fergusonite; $Y(Nb,Ta)O_4$	Evje, Norway; granite pegmatite	0.8	2.4	0.1	0.5	1.7	-	6.6	1.5	21	5	20	3.4	31	5.8	-
71	Fergusonite; $Y(Nb,Ta)O_4$	Sabaragamuva; Ceylon; granite pegmatite	1.2	3.	1.3	4.7	8	0.5	15	2.5	16	3.8	17	3.2	20	3.8	-
72	Fergusonite; $Y(Nb,Ta)O_4$	Keivy; alkali granite pegmatite	5.7	14	1.1	3.3	7	1	13	2.3	13	3	14	2.7	16	3.5	b)
73	Hellandite: $Ca_2Y_3Al_3(SiO_4)_4(O,OH)_4$	Kragero, Norway: granite pegmatite	2	5.8	1.5	4.8	4	0.2	12	2.2	17	4.1	14	2.1	26	4.1	b)
74	Zircon; $ZrSiO_4$	N.Tuva; albitite of alkali syenites	1	3.5	0.7	1.5	1.7	0.2	3.5	0.8	15	4	23	3.6	36	5.8	t)
75	Zircon; $ZrSiO_4$	Zhdanov Alkali Massif, Ukraine; albitite	1.8	5.8	1.4	3.3	3.1	0.2	7.8	1.6	23.4	5.8	19.5	3.1	19.5	3.7	-
76	Zircon; $ZrSiO_4$	Sorug, N.Tuva; nepheline syenite pegmatite	1.7	27.2	7.3	25	8.3	0.6	6.9	1	6.1	1.5	7.3	1.5	4.8	0.8	-
77	Spessartite; $Mn_3Al_2(SiO_4)_3$	Keivy; alkali granite pegmatite	2	7	0.9	2	0.4	-	1.6	0.5	6.5	2.1	14	2.2	53	8	-
78	Siderite; $FeCO_3$	Aryskan, N.Tuva; albitite of alkali syenites	-	-	-	9	6.6	-	14.6	2	34.7	-	24.3	-	9	-	-
79	Thortveitite; $(Sc,Yb)_2Si_2O_7$	Madagascar; granite pegmatite	-	-	-	-	0.5	-	5.4	1	8	2.2	9	1.6	61	11	b)

Table 1. Composition of Rare Earths in Minerals ($\Sigma TR_2O_3 = 100\%$) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
80	Thortveitite; $(Sc,Yb)_2Si_2O_7$	Madagascar; granite pegmatite	2	8	3	-	-	-	-	-	17	4	12	2	44	8	-
81	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Vishnevye Gory; alkali syenite pegmatite	15	52	7	16	2.3	0.2	3	0.4	2.1	0.4	0.7	0.1	0.9	0.2	-
82	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Ilmeny; alkali syenite pegmatite	14	48	7.3	22	3.1	0.1	1.8	0.2	1.8	0.4	0.9	-	0.4	-	b)
83	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Tatarka, Enisei Range; alkali syenite pegmatite	2.2	13	6.7	22	17	2	13	2.5	11	1.5	5.5	0.8	2.2	0.5	e)
84	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Ilmeny; hydrotherm of granites (the extreme of 40 specimens of La type)	41.1	44.9	3.4	9.6	1	-	-	-	-	-	-	-	-	-	i)
85	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	N.Carolina, USA; granite pegmatite (the extreme of 40 specimens of Nd type)	18.3	41.9	5.3	22.2	7.7	-	4.6	-	-	-	-	-	-	-	a)
86	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kalai-Makhmud River, Turkestan Range; granite pegmatite	24	48	5.8	19	2	0.1	0.8	0.1	0.4	-	-	-	-	-	-
87	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kuramin Range; granite	23	55	6	14	0.9	0.1	0.6	-	0.1	-	0.1	-	0.6	-	s)
88	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	S.Yakutiya; para-gneiss	24	59	3.6	13	0.3	-	-	-	-	-	-	-	-	-	v)
89	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Keivy; alkali granite pegmatite	22	54	6	15	1.2	-	0.5	- -	0.4	0.1	0.3	-	0.6	0.1	-
90	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kamennaya Taibola, N.Karelia; granite pegmatite	14	32	6.5	17	7.4	0.4	10	2	6.2	1.3	1.7	0.2	1.1	0.3	-
91	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Sinyaya Pala, N.Karelia; granite pegmatite	1.3	2.2	0.2	0.4	1.1	0.2	15	2.7	2.7	6.5	17	2.7	20	4.1	-
92	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Vishnevye Gory; alkali syenite pegmatite	22	59	5.1	12	1.3	0.1	0.3	-	-	-	-	-	-	-	-
93	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Korarfvet, Sweden; granite pegmatite	5	20	5.2	14	9.5	0.7	8	1.8	15	3.2	7	1.2	8	1.4	ad)
94	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Impilakhti, S.Karelia; granite pegmatite	4.2	16	4.3	11	8.8	0.4	8.6	2	15	2.8	10	1.5	13	2.5	y)
95	Pyrochlore; $(Na,Ca,TR)_2$	Alakurtti, N.Karelia; granite pegmatite	3	11	3	12	22	0.5	25	4	13	1.5	2.5	0.5	1.7	0.4	z)

Item No.	Mineral and formula	Source and geologic features	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Remarks
96	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Yauri-Ioki, Kola Peninsula; greisen	1.8	6.2	3.5	10	9	0.2	11	2.3	16	3.5	14	2.6	17	2.8	aa)
97	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	N.Caucasus; granite pegmatite	2.3	9	4	14	10	0.2	12	1.9	14	3	10	1.8	15	2.9	ab)
98	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Hitterö, Norway; granite pegmatite	2.1	6.5	2.8	8	9	0.3	19	3.1	16	3.1	11	2	15	2.3	-
99	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Iveland, Norway; granite pegmatite	1.6	5	2	6.5	9.3	0.3	18	2.5	17	3.5	13	2.3	16	2.1	-
100	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	0.9	3	2.9	7	8	0.3	19	2.8	17	3.5	12	2	18	2.9	-
101	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.4	3.5	1.5	5.4	7.5	0.5	18	2.9	17	3.7	14	2.5	19	3.1	-
102	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Birkeland, Norway; granite pegmatite	1.4	3.7	1.7	6	8	0.2	13	2.4	37	4	8	1.2	12	1.7	-
103	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Birkeland, Norway; granite pegmatite	0.9	2.5	2	6.5	9	0.4	22	3.6	20	4	13	2	12	2	-
104	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	N.Yakutiya; alkali granite pegmatite	4.2	10	1.5	4.7	3.7	0.3	10	2	22	4.8	15	2.5	17	2.7	ac)
105	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	2.5	7	3.5	8	7	0.2	16	2.6	15	3.3	11	1.5	19	3.3	b)
106	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.2	4	2.5	7	8	0.3	18	2.7	17	3.5	12	2	19	3	-
107	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	3.4	12	5.7	12	5.8	0.3	8	1.6	13	2.6	12	1.9	19	2.8	b)
108	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Keivy; alkali granite pegmatite	5.8	19	3.3	7	1.8	0.1	2.6	0.5	7.1	1.9	12.6	2.2	31	4.8	-
109	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.7	6	2.6	9	8	0.3	12	2	13	2.7	11	2	25	4.5	-
110	Britholite; $TR_6Ca_4Si_2O_{24}(OH)_2$	Khodzha-Achkan River, Turkestan Range; alkali syenite pegmatite	28	52	6	13	0.4	-	0.4	0.1	-	-	-	-	-	-	ae)
111	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Khibiny; apatite-nepheline rocks	24	48	6.1	18	1.7	0.2	1	-	0.6	0.1	0.2	-	-	-	-
112	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Lovozero; ijolites	22	51	5.9	17	1.7	0.2	1.6	0.2	0.4	-	-	-	-	-	-
113	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Lovozero; alkali syenite pegmatite	21	45	6.8	21	3.7	0.3	1.2	0.1	0.3	-	0.3	-	0.2	-	-
114	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Sumy District, Ukraine; phosphates	18	42	6.3	21	4	0.3	4	0.6	2	0.3	1	0.1	0.4	0.1	-
115	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	N.Caucasus; phosphates	13	34	5.5	19	7	1.5	8	1.3	4.7	0.9	2.6	0.4	1.7	0.4	-
116	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Podolia, Ukraine; phosphates	6.5	23	7.5	2.6	13	2	13	2	4.2	0.8	1.4	0.1	0.6	0.1	-
117	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Elovka, Transbaikal; granite pegmatite	5.1	11.4	4.4	6.8	24.1	0.7	26.8	4	9.8	1.9	2.1	0.9	1.3	0.7	af)
118	Chindusuite; $mMnO_2 \cdot nTiO_2 \cdot pSiO_2 \cdot qH_2O$	Lovozero; sodalite syenite pegmatite hydrothermal stage	3.1	21	6.8	25	12	1.4	9.5	1.6	9	1.9	4.1	0.8	2.9	0.6	-
119	Halloysite; $Al_4Si_4O_{10}(OH)_8 \cdot 4H_2O$	Lovozero; nepheline syenite; hydrothermal stage	26	20	7	25	5.4	1	5.3	0.9	3.9	0.8	2.1	0.3	2	0.4	-

Table 1. Composition of Rare Earths in Minerals (ΣTR_2O_3 = 100%) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
120	Apophyllite; $KCa(Si_4O_{10})_2F\cdot H_2O$	Lovozero; nepheline syenite pegmatite	17	33	6.1	21	6	0.6	5.8	0.8	4	1	2.4	0.2	1.7	0.3	-
121	Fluorite; CaF_2	Keivy; alkali granite pegmatite	5	10	1.1	3	2.8	0.2	2	0.5	7	2	16	2.5	41	7	-
122	Fluorite; CaF_2	Kara-Oba, Kazakhstan; hydrotherm of granites	2.2	6.5	1.7	5.9	5	0.2	11	1.7	14	3.3	13	2.8	28	4.6	ag)
123	Fluorite; CaF_2	Hundholmen, Norway; granite pegmatite	4.3	13	3.7	9	4.7	0.3	10	2	13	3	13	1.9	19	3.3	-
124	Andradite; $Ca_3F_2(SiO_4)_3$	W.Transbaikal; Skarns	9	21	8	14	3.8	0.2	4.7	1	10	2.2	9	1.7	13	2.5	ah)
125	Scheelite; $CaWO_4$	Kara-Kamys, E.Kazakhstan; hydrotherm of granites	13	40	7.2	17	9.6	1.3	5.8	0.9	3.1	0.8	1	0.1	0.4	-	-
126	Sphene; $CaTiSiO_5$	Khibiny; sphene-apatite-nepheline rocks	20	45	6.5	21	3	0.3	2.3	0.3	1	0.2	0.4	-	0.2	-	-
127	Sphene; $CaTiSiO_5$	Yakutiya; para-gneiss	13.5	48	8.7	21	4.3	0.3	1.6	0.3	0.8	0.2	0.5	-	0.6	0.1	v)
128	Sphene; $CaTiSiO_5$	Borshchevochn. Range, Transbaikal; granites	7	23	10	27	9.4	0.8	7.8	0.9	6	1.3	2.5	0.4	3	0.6	ai)
129	Sphene; $CaTiSiO_5$	Iveland, Norway; granite pegmatite	2.5	8	2.5	9	7	0.7	18	2.5	17	3.6	12	1.5	14	2	aj)
130	Sphene; $CaTiSiO_5$	Iveland, Norway; granite pegmatite	1.6	5.8	3.8	11	6	0.5	9.3	1.5	11	2.7	13	2.5	26	5	aj)
131	Eudialyte; $(Na,Ca)_4 FeZr (Si_6O_{18}) (OH,Cl)$	Lovozero; nepheline syenite pegmatite	19	42	6	20	3.3	0.3	2.5	0.5	2.5	0.4	2.1	0.2	1.1	0.2	-
132	Eudialyte; $(Na,Ca)_4 FeZr (Si_6O_{18}) (OH,Cl)$	Lovozero; eudialyte luyavrite	14	37	5.7	17	6	0.8	6	0.8	4.7	0.8	3.6	0.6	2.6	0.4	- -
133	Eudialyte; $(Na,Ca)_4 FeZr (Si_6O_{18}) (OH,Cl)$	Lovozero; sodalite syenite pegmatite	11	35	7	22	7.2	1.6	6.7	1	4.4	0.9	1.9	0.4	0.5	0.2	-
134	Eudialyte; $(Na,Ca)_4 FeZr (Si_6O_{18}) (OH,Cl)$	Botogol, Buryat-Mongolia; alkali syenite pegmatite	11.1	18.9	3.2	8.9	3	0.5	5.7	1.1	14.8	4	14	2.4	10.5	1.9	ak)
135	Thorianite; ThO_2	Ceylon; Placers	10	41	9	25	6.3	0.3	3.1	0.5	1.9	0.5	0.8	0.2	1.1	0.2	-
136	Uraninite; UO_2	Chupa, N.Karelia; granite pegmatite	0.6	1.3	1	4	12	0.7	19	3.7	21	4	13	2.7	14	2.7	-
137	Thorite; $ThSiO_4$	Lovozero; nepheline syenite pegmatite	22	55	6	15	1.9	-	0.3	-	-	-	-	-	-	-	-
138	Epidote; $Ca_2Al_3(Si_2O_7)(SiO_4)O(OH)$	Talitskii Massif, Altai; granite	17.3	41.2	4.9	16.8	3.8	0.5	4.7	0.8	3	0.8	3.6	0.7	1.4	0.3	al)

Remarks on Table 1

) According to Murata et al. (b) "Mineral." (c) According to A.V. Kosterin
d N.V. Turanskaya. (d) N.V. Turanskaya, Analyst. (e) Collected by I.P. Tik-
nenkov. (f) Collected by E.M. Eskova. (g) Collected by O.V. Krashennikov.
) According to N.V. Turanskaya and Yu. S. Slepnev. (i) According to E.E.
inshtein et al. (j) Collected by E.I. Dolomanov. (k) "Khlopinite" (also chlop-
ite, propably Ti-poor euzenite). (l) "Ampangabeite." (m) Mineral: "ampanga-
ite." (n) Mineral; collected by V.A. Kornetova. (o) Collected by V.B. Alexan-
ov. (p) "Blomstrandite" (probably betafite). (q) Collected by V.I. Noneshnikova.
Collected by Yu. P. Ivenson. (s) Mineral; collected by I.E. Smorchkov. (t)
rtolite; collected by V.B. Alexandrov. (u) Collected by V.B. Alexandrova; ana-
zed by N.V. Turanskaya. (v) Collected by V.A. Galyuk. (w) Collected by A.N.
buntsov. (x) "Toerneboehmite." (y) Collected by A.P. Kalita. (z) Obruchevite;
llected by A.P. Kalita (yttrian pyrochlore). (aa) Collected by I. Kupriyanova.
) Collected by G.D. Afanasev. (ac) Mineral; collected by E.G. Troshchenko.
l) "Hjelmite". (ae) Collected by V.I. Stepanov. (af) Collected by Z.V. Vasileva.
) Collected by L.P. Ermilova. (ah) Collected by E.A. Nechaeva. (ai) Collected
N.I. Zabavnikoa. (aj) "Yttrotitanite". (ak) Collected by K.A. Zhuk-Pochekutov.
) Collected by V.V. Lyakhovich.

he analyses in the table are grouped as follows:

Nos. 1 through 19 - Selectively cerium minerals;
Group 1a: Markedly selective cerium minerals.
Nos. 20 through 40 - Selectively cerium minerals;
Group 1b: Selectively cerium minerals.
Nos. 41 through 45 - Group 2: Selectively gadolinium minerals.
Nos. 46 through 78 - Group 3: Selectively yttrium minerals.
Nos. 79 through 80 - Group 32: Selectively yttrium-ytterbium minerals.
Nos. 81 through 138 - Group 4: Complex minerals.

(A) CLASSIFICATION OF RARE EARTHS ACCORDING TO COMPOSITION

Analysis of the data on composition of the rare earths may be
cilitated considerably by the use of graphic methods. For example,
ere is the well known method of a diagrammatic representation of
TR composition by means of a broken line connecting the points
dicative of both odd and even lanthanide compositions (Fig. 1a) (Pm
ay be omitted here, because of its absence from the earth's crust).
wever, the pattern becomes far more interesting if two curves are
awn, instead of one, for the odd and the even lanthanides respec-
ely (Fig. 1b) [12]. Such curves, as one may see, are generally
mple and smooth and they have only a few peaks (1 or 2, as a rule).
These curves so drawn are true images of the odd and the even
thanide curves. Indeed, the Dy maximum on the even TE curve is
logous to the Ho maximum on the odd TR, as Dy is right next to Ho.
same holds also for the Sm-Er couple on the aeschynite TR curve

(Fig. 1b). The Sm and Er minima are analogous to the Eu and Tm minima, etc. Therein lies apparently an expression of a direct relationship, a correlation, between the proportions of the odd and the even elements (neighbors of each other in the table) in the following couples: Ce-La; Nd-Pr; Sm-Eu; Gd-Tb; Dy-Ho; Er-Tm; Yb-Lu. This odd-even correlation between the coupled elements enables us to represent both the even and the odd (its cognate) element by one single point on the horizontal curve. Analogies of the odd and the even TR elements are made conspicuously clear by the diagrams constructed for the purpose (Fig. 2).

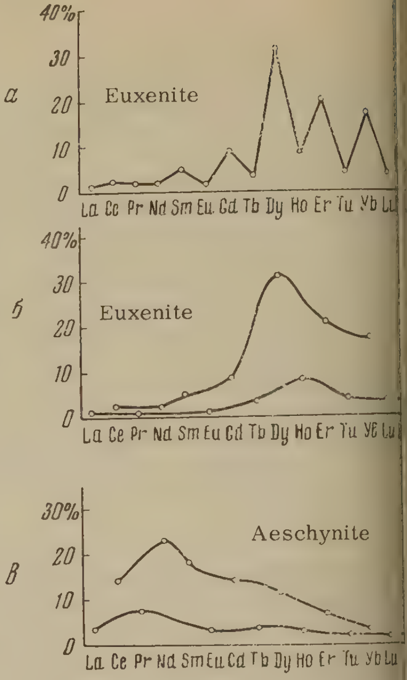

Fig. 1. Different methods of representing composition of the rare earths.

The TR composition curves may be classified as "simple" (Figs. 2a, 2e) or "complex" (Fig. 21), depending on their shape. There is only one peak in the simple curves, but there are several peaks in the complex curves. The simple curves have only one arm, if their peaks represent Ce or Yb, but two arms in all other instances. The simplest of the simple curves may be approximated as single simple continuous functions. For example, the even lanthanide curves for loparite (cerian perovskite) or fergusonite (Figs. 2a, 2i) may be represented crudely by a descriptive function of the type of $C = C_0 \times 10^{K(Z_0 - Z)}$.

In this case, "C" and "Z" stand for the concentration and the atomic number of the element in question, with "C" as the maximum; K is the tangent of the slope angle of the $C = f(z)$ curve which is a line on the logarithmic scale. For loparite, $K = 0.127$ and $Z_0 = 70$.

The even curve for samarskite (Fig. 2e) may be approximated by a function of the type $C = \frac{C_0 \times A^2}{(Z - Z_0)^2 + A^2}$, where "A" is one half of the breadth of the curve at one half of its maximum. In this particular case, $A = 1.27$ and $Z_0 = 64$. Inasmuch as the even and the odd element curves are similar, their descriptive functions tend to resemble each other.

The community of fortunes of individual elements in the lanthanide group, their "trans-migrations" only by groups, "chain"-like, the conjugation of the even and the odd elements, so clearly visible in the curves showing proportions of the lanthanides not only in the minerals

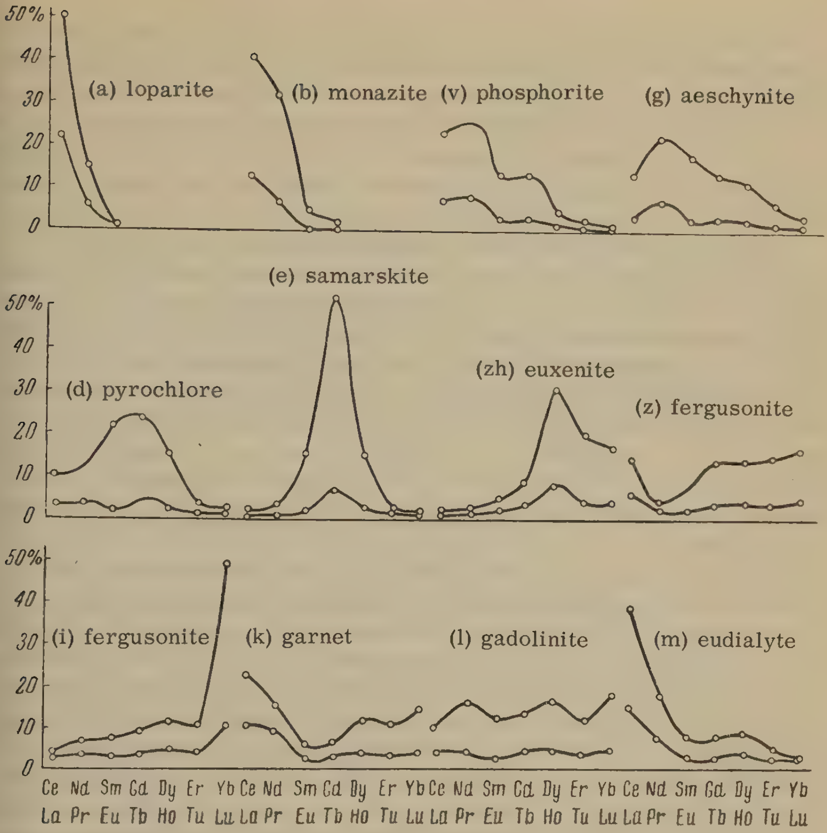

Fig. 2. Composition of rare earths in different minerals.

t also in the chemically separated sums of the rare earths (Fig. 5), e plainly visible in the curves. This means that the fundamental lationships governing distribution of the rare earths are the same th for the mineralogic and for the chemical materials.

The averages of ionic radii, atomic weights, neutron-capture cross-ctions, etc., are among the major (diagnostic) characteristics, in the stance of the rare-earth minerals and of the groups of the rare rths themselves. Thus the average ionic radius of the lanthanide oup may be represented as:

$$r_{\text{ave.}} = \frac{(r_{La} \times C_{La}) + (r_{Ce} \times C_{Ce}) + \dots}{100} = \frac{\Sigma r_i c_i}{100},$$

ere r_i is the ionic radius of the element and c_i is its concentration the ΣRE_2O_3. The $r_{\text{ave.}}$ is at its maximum, 1.02 Å, for the bast-esite lanthanides (No. 1 in the table). The lowest r_i, 0.82 Å, is observed in the lanthanides of thortveiteite, where it is very close to the radius of Yb. The average atomic weight of the lanthanides in bastnaesite and thortveitite is 140 (like Ce) and 167 (like Er) respectively.

The effective average maximum neutron-capture cross-section, for slow neutrons, is shown by the samarskite rare earths (No. 41) and is 24980 barns; the minimum, 40 barns, is shown by the bastnaesite rare earths (No. 1).

V. Goldschmidt and L. Thomassen [1] proposed two categories in their classification of the rare earths in minerals according to composition, the "complex" and the "selective".* The greater the maximum on the composition curve, the greater is the "selectivity" of the composition. Depending on the size of the maximum, one may distinguish the following types of composition: markedly selective (> 45 to 50%); selective (> 30%); complex (< 30%). In addition to the size of the maximum, the degrees of selectivity may be characterized also by the "K" and the "A" coefficients from the equations previously cited. The smaller the "A", the greater the "K", — the more selective the composition.

The composition curves are simple, in the case of the selective (especially the markedly selective) categories of the rare earths, with only one single maximum and with steeply sloping arms. In the case of the complex category, the composition curves are complicated and they contain several maxima (weakly expressed, as a rule). Serious difficulties arise occasionally in deciding whether the rare-earth composition in question should be referred to the selective or to the complex category.

Typically selective or markedly selective compositions are most characteristic, occupying extreme positions in the lanthanide series (Ce and Yb). Elements in the intermediate positions in this series present a more complicated case. Thus curves of the type shown in Figure 2d have practically identical maxima for the two neighboring even elements, Gd and Sm. Such compositions are weakly selective with respect to these two elements, but are highly selective at the same time, with respect to the small part of the rare-earths "spectrum" from Sm to Gd, inasmuch as their content of lanthanides outside the limits of this part of the "spectrum" falls off abruptly. The TR compositions of this type, represented by simple curves, may be classified rationally as samarium-gadolinium selective ones, since the typically or the markedly selective gadolinium compositions are exceptionally rare. The broad cerium-neodymium TR maximum was noted in zircon No. 76; the samarium-neodymium maximum in aeschynite No. 83; the dysprosium-gadolinium in samarskite No. 44; the erbium-dysprosium in zircon No. 75.

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*The complex category includes compositions with relatively uniform proportions of the lanthanides; the selective category, compositions in which one or more of the lanthanides are definitely preponderant.

In the instance of the "m" type curves, Figure 2, there is also a supplementary Dy maximum in addition to the principal maximum of Ce. It is clear a composition of this type is not particularly selective, and yet it may be hardly called complex, because the main maximum is so definitely preponderant over the supplementary one.

The "wave-like" pattern is characteristic of the transition from a selective composition (one maximum) through a complex composition to another selective composition (one maximum) (Fig. 3, Curves 1 through 5). As the degree of selectivity becomes smaller, the slopes of the curves become progressively less steep, to the point where any further flattening-out of the main peak becomes impossible without a break in the smoothness of the curve. When that happens, a minimum makes its appearance on the curve, together with a hint of a new supplementary maximum which grows bigger as the first (main) maximum flattens out.

Up to this time, in minerals, we knew of the selective rare-earths' compositions with the Ce, the Dy, and the Yb maxima (Fig. 2b, 2zh, 2i respectively). As shown both in the table and in Figure 2, however, there are minerals in nature whose rare earths have the Nd and the Gd maxima (Fig. 2g, aeschynite, and Fig. 2e, samarskite, respectively). Thus we find cerium, neodymium, gadolinium, dysprosium, and ytterbium compositions of the lanthanides in the minerals.

The content of Sm and Gd which falls on the maximum in the curve is about the same in some specimens of samarskite. In zircon (No. 75) the Er content is also rather close to the maximum. This leads us to the idea that there may be some rare earth minerals in nature with the composition maxima embracing all of the even elements: Ce, Nd, Sm, Gd, Dy, Er, Yb. However, the relative abundance of minerals with this or that kind of maxima in the composition curve is highly variable. The most common ones are the minerals with the cerium maximum. Yttrium minerals have generally the Dy and the Yb maxima in their lanthanides. Minerals with the Gd and the Nd maxima are far more rare. No minerals could be discovered so far with clearly defined Sm and Er maxima. The foregoing considerations suggest the following sequence of the relative abundance of the composition maxima for the even lanthanides in minerals:

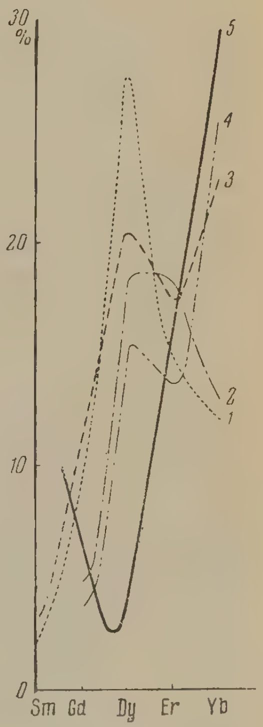

Fig. 3. The "wave pattern" of transitions from one maximum to another.

Ce, Dy, Yb, Gd, Nd, Er, Sm. The relative abundance of the composition minima is in the reverse order of this sequence.

The abundance sequence of the maxima for the odd elements is analogous to that of their even cognates: La, Ho, Lu, Tb, Pr, Tm, Eu. The relative abundance of the elements themselves is characterized also by their maximum concentrations (per cent): 42.9 La; 59 Ce; 9.5 Pr; 33.6 Nd; 22 Sm; 1.6 Eu; 5.3 Gd; 6 Tb; 37 Dy; 7.6 Ho; 23 Er; 5.4 Tm; 61 Yb; 11.6 Lu. Thus, if this percentage exceeds 50 for Ce, Yb, and Gd, it does not attain even 10 for any of the odd elements, with the exception of La.

The clarke relationships of the elements are reflected, to some extent, in the abundance sequences of the lanthanide composition maxima in minerals, as well as in the percentage concentrations represented by such maxima on the composition curves. Indeed, the fact that Sm, Eu, Er, and Tm never yield any maxima on the composition curves, and are generally in the minima, indicates that these elements are extremely deficient in the earth's crust.

We must take into account nevertheless the content of the given element in minerals in which the maximum is represented by some other element, as we now pass to a discussion of the clarke sequence of the lanthanides. Thus, although there are very few minerals showing an independent neodymium maximum, large amounts of Nd are present in the abundantly distributed cerium minerals. We are justified therefore in placing Nd next to Ce, with respect to its relative abundance. The same reasoning may be followed also for certain other lanthanides.

Further statistical data on composition of the rare earths in minerals and on the relative abundance of the minerals themselves may serve apparently in verifications and corrections of the sequences here stated as well as of the currently accepted relationships between the lanthanide clarkes in the earth's crust.

Among the cerium type compositions of the rare earths in minerals, we may distinguish three types: the normal, the cerium anomalous, the cerium-free anomalous. The vast majority of the minerals have their TR's of the normal type. Such minerals are characterized consistently by the relationships already reported [3, 4, 5]: the relatively constant proportions of cerium (about 40 to 50%) and of praseodymium (about 5%); the inversely proportional relationship betwee La and Nd (La + Nd approx. constant). Anomalous minerals with tetravalent cerium are also known whose TR consist almost entirely of cerium. Cerianite, CeO_2, is one of these; it was first discovered in endogenic carbonatite deposits in Canada. We ascertained composition of the TR in cerianite which was formed on a weathering of bastnaesite in pegmatites of Madagascar. Its composition is as follows: $La_6Ce_{91}Pr_{.09}Nd_{2.1}$. Since this test material is ocherous, one might think that the presence of La, Pr, Nd is due to a contamination. However, it has been proved experimentally that there exists a series of solid solutions $(Ce^{VI}, Th, U) O_2 — TR_2O_3$. Characteristically, there is no enrichment of Pr in cerianite, because, in this particular case, there is apparently no formation of Pr^{IV}.

Thus cerianite is practically 100% the oxide of one single element—Ce. We are dealing here not only with a complete rupture of rigid bonds (La + Nd about constant) characteristic of ordinary cerium compositions but also of the common chain bonds, so characteristic of the trivalent rare earths. The decisive preponderance of cerium over lanthanum may be illustrated by zircon (No. 76) and by several other minerals.

The most recently published data of Hildebrand [10] on a most curious rhabdophane of the cerium-free anomalous composition of its TR, from Connecticut, USA show: $La_{37.6}\ Ce_{0.8}\ Pr_{0.8}\ Nd_{44.4}\ Sm_{7.5}\ Eu_{1.5}\ Gd_{7.4}$. This rhabdophane contains practically no cerium or praseodymium, in contrast with the other cerium minerals. These two elements had passed apparently into their anomalous tetravalent forms and were parted as an independent phase, $(Ce, Pr)O_2$.

Curiously, the lanthanide chains were not disturbed in this rhabdophane, despite the lapse of two elements (Ce and Pr) from the lanthanide series, between lanthanum and neodymium.

The following anomalous TR composition was established for halloysite (No. 119): $La_{26}\ Ce_{20}\ Pr_7\ Nd_{25}$. Lanthanum here is higher than cerium or any other element, so that, in the case of this sort, we may speak of the lanthanum maximum of the TR in minerals. However, we do not yet recognize a distinctive lanthanum type of the rare earths, inasmuch as the case in question is the first one of the kind and still remains to be studied in detail. This halloysite example is an illustration of an incomplete withdrawal of cerium, as against its nearly complete withdrawal in the instance of the rhabdophane. In cerium-free anomalous minerals of this type, there is a disturbance of the analogy between the even and the odd lanthanide curves and these curves intersect each other.

For a series of minerals (fluorite, strontianite, pyromorphite, microcline, etc.) there were frequent reports on an enrichment by europium, as evidenced by optical spectrographic data. Europium is present in such minerals in its divalent state and replaces Sr, Pb, and K, resembling them in the size of their ionic radii. However, we found about the same amounts of europium in the minerals we had examined, both strontium (nordite, fluorite) and lead (anglesite), as are present in ordinary cerium minerals. The reports on the specific role of europium in some minerals may be attributed frequently to the fact that spectrographic optical analysis is most sensitive for this particular lanthanide.

(B) LANTHANIDE COUPLES

More than three quarters of the total rare earths in minerals consist generally of the even elements which play a leading part, in many respects, and by which the fortunes of the odd elements are also determined. The content of an odd element is higher in proportion to the content of its even neighbors. However, this even-odd correlation is generally more close between the given odd element and some particular one of its even neighbors. The following correlations are indicated by the analysis: Ce-La; Nd-Pr; Sm-Eu; Gd-Tb; Dy-Ho; Er-Tm; Yb-Lu In such manner the odd elements to the left of Pm, in the rare-earth series (with "z", the atomic number lower than 61) are correlated wit their even neighbors on the right, whereas the odd elements to the righ of Pm ("z" higher than 61) are correlated with their even neighbors o the left.

Such grouping of the couples is sustained most convincingly by Figure 4 and by the analogy between the curves for the even and for the odd lanthanides constructed on the basis of the principle of their coupling, as here formulated (Fig. 2). There is no correlation and no analogy between the curves, if we group the lanthanide couples differently (e.g., Yb-Tm, Er-Ho,etc.). Characteristically also, chemically (first of all, chromatographically), in the separation of the couples, the greatest difficulties arise in the cases of Nd and Pr, Sm and Eu, Yb and Lu.

The following characteristic ratios within the lanthanide couples are indicated by the general averages for all of the minerals: Ce:La = 3; Nd:Pr = 3; Gd:Tb = 6; Dy:Ho = 5; Er:Tm = 6; Yb:Lu = 6. The Sm:Eu ratio is very much higher and may be given tentatively as 10 to 20. One fact stands out conspicuously, namely: Ce:La ≈ Nd:Pr; Gd:Tb ≈ Dy:Ho ≈ Er:Tm ≈ Yb:Lu. A breakdown of the rare-earth series into two sections is

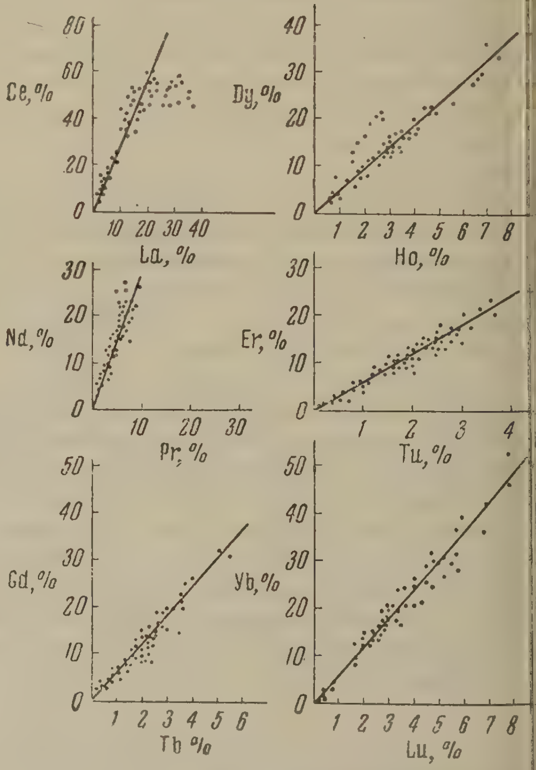

Fig. 4. Proportions of odd and even lanthanide

indicated accordingly (La to Nd and Gd to Lu); this break is at the Sm - Eu couple, immediately next to Pm ($z = 61$). It is possible that these two sections of the lanthanide series were formed by two different branch-variants of the nuclear process.

The phenomenon of the lanthanide couples may be explained possibly by the similarity of the ionic radii of the couples. According to N. V. Belov and G. B. Bokii, their ionic radii are as follows: La - 1.04, Ce - 1.02; Pr - 1.00, Nd - 0.99; Sm - 0.97, Eu - 0.97; Gd - 0.94, Tb - 0.89; Dy - 0.88, Ho - 0.86; Er - 0.85, Tm - 0.85; Yb - 0.81, Lu - 0.80 Å. It is evident therefore that the ionic radii are about the same for Lu and Yb, Pr and Nd, and are equal for Tm and Er, Eu and Sm.

The approximate equality of the ionic radii in the lanthanide couples may be related to the similar distribution of their 4 f electrons in their orbits which is not the same for elements belonging to different couples (thus Yb and Lu have fourteen f electrons each). Curiously, there is no coupling on the basis of atomic radii in the lanthanides. Consequently, the phenomenon of the lanthanide couples is characteristic apparently for compounds with ionic bonds.

The diagram in Figure 4 shows that the Ce - La correlation has been definitely weakened. We also know of examples where La > Ce [11]. This may be due to the "extreme left" position of La in the rare-earths series, to the point that La is the only one of the rare earths that has no 4 f electrons. Moreover, the anomalous La-Ce relationships may be caused by the capacity of cerium to assume the tetravalent state.

Insofar as the degree of similarity between the ionic radii of the lanthanide couples is not the same, there may be differences also in the extent of their correlations. After conclusive determinations of their ionic radii and of their electronic configurations, it should be highly desirable to ascertain the relationship between their atomic proportions and the ionic radii. It should be interesting also to find out whether there is a coupling among the actinides which resemble the lanthanides.

The characteristic ratios between the even and the odd lanthanides obtained by analysis of the rare earths in minerals are apparently very close to the ratios of their clarkes. This enables us to utilize these ratios in minerals in correcting the currently accepted lanthanide clarke ratios. For example, V. M. Goldschmidt's clarke ratio Yb:Lu = 3.5 is too low, in all probability, while his Er:Tm = 12 ratio is too high. Curiously, F. Clarke reports Er:Tm = 5.

The analogy between the curves of the even and of the odd lanthanides (expression of the diagnostic relationships), and the smoothness and the common simplicity of these curves are indicative of the correctness of the analyses of the rare earths in minerals. A whole series of old decipherings by many others pretending at a quantitative reliability of their results, should be treated now only as qualitative findings, because they fail to meet the required criteria. The characteristics of the lanthanide composition curves, as shown here, justify extrapolations, in the instance of the selective compositions.

The ratios between the coupled even-odd lanthanides are only approximately constant. For example, although the normal Er:Tm = 6, this ratio may vary from 4.5 in samarskite to 7.5 in eudialyte, i.e., more than 1.5 times. The typical lanthanide ratios are most commonly observed in compositions of the complex type which are represented by complex curves with several gently sloping maxima. For example, the Er:Tm ratio is fairly constant and is approximately 6 for all gadolinites whose lanthanides are of the complex type (Nos. 97-109 in the table).

The widest variations in the ratio of the coupled even-odd lanthanides are observed in the TR compositions of the selective type. For example, Gd:Tb = 8 and Dy:Ho = 9 in a samarskite with a strong gadolinium maximum (No. 41 in the table), whereas Yb:Lu = 4.5 and Er:Tm = 4.5. The first two of these ratios are apparently characteristic for elements at their maxima and the too-low ratios for elements at their minima, in curves representing composition of the markedly selective type. The excessively low ratios may be compensated, in some cases, by some excessively high ones but may be tied, in some other cases, to a constant ratio between the total even and the total odd lanthanides. Indeed, the sum-total of the even elements remains fairly constant, in the vicinity of 85% (of Σ TR), in many minerals, excepting cerium minerals.

The selective compositions show occasionally that an odd lanthanide may be influenced by an even one, both within and outside the even-odd couple. Thus, in the two examples of the lanthanide compositions in fergusonite (Nos. 65 and 72 in the table), Tm is relatively high in the very same lanthanides (No. 65), which show also a markedly high ytterbium maximum. This may be explained by the position of Tm, intermediate between Er and Yb in the rare earths series. Although Tm is generally correlated with Er, the abrupt rise in the Yb content brings about an increase in the content of its neighbor, Tm, but not of Er. On the contrary, in the case of a markedly high dysprosium maximum, the Er:Tm ratio rises above its ordinary level.

In such manner, if the maximum in the selective composition is to the right of the couple in question, the ratio within the couple falls below its ordinary level; if the maximum is to the left—the ratio within the couple increases.

We must take into account the fact that the characteristic ratios between the coupled even and odd elements are subject to smaller variations at different TR compositions in one and the same mineral than in several different minerals. For example, in fergusonite: Er:Tm $\approx$ 6 and Yb:Lu $\approx$ 5.4 show very little variation. On the other hand, the abnormal Dy:Ho = 9 ratio is found both in the selectively gadolinium mineral, samarskite, and in the gadolinium-type TR composition of an entirely different complex mineral, pyrochlore. Thus not only the crystal structures but also the TR compositions, that is, positions and size of their maxima, play a decisive part in establishing the ratios between the coupled lanthanide elements.

(C) CLASSIFICATION OF RARE EARTH ELEMENTS

As we know, Sc and Y (atomic numbers 21 and 39 respectively) are often included with the lanthanide group consisting of 15 similar elements, from La through Lu (atomic numbers 57 and 71 respectively). Indeed, there exist minerals containing Sc and practically no lanthanides, such as cassiterite and wolframite. Also, most of the lanthanide minerals, and especially the cerium group, contain no Sc.

The Y problem is more involved. All of the known yttrium minerals contain lanthanides, whereas most of the lanthanide minerals (not all) contain Y. The lanthanides amount only to about 30% of the rare earths in xenotime, euxenite, fergusonite, and many other minerals, whereas 70% of the ΣTR_2O_3 is Y itself functioning as the leading or the principal element. We must refer to such minerals therefore as yttrium minerals and not as dysprosium or ytterbium minerals.

As we know, the ionic radius of Y is similar in its size to the ionic radii of Dy and Ho and that it is for this reason that the fractionation of this group is particularly difficult in chemistry. There is every indication that it is feasible to treat Y as a member of the lanthanides, in mineralogical and geochemical research, and to deal with the rare earths (TR) as with a combination of the lanthanides (''Ln'') and yttrium.

Very small quantities of yttrium are present not only in the cerium but also in the neodymium (aeschynite) and the gadolinium (samarskite) minerals. On the other hand, yttrium is preponderant in the rare earths with the Dy and the Yb lanthanide maxima. There is a direct correlation apparently between Y and the heavy lanthanides (Dy, Ho, Er, Tm, Yb, Lu) with the ratio of Y:Σ (Dy-Lu) approximately equal to 3. Characteristically, in this connection, the Y content is high in the eudialyte rare earths, on account of the enrichment of this mineral with heavy lanthanides. There is a lowering of the Y-heavy lanthanides ratio in the TR compositions whose maxima of the center fall on (Gd, Dy).

A correlation with certain specific lanthanides is indicated also for Sc. The rare earths in thortveitite, the principal scandium mineral Nos. 79 and 80) have their maximum characteristically at Yb. According to Wylie [7], the Australian fergusonite is significantly enriched with Sc and its lanthanide maximum falls on Yb. Thus a definite association is noted for Sc and Yb specifically, and not for Sc and the yttrium earths. This relationship was first suggested by T. Sahama and V. Vahatalo [6] who discovered Sc ''highs'' in Yb-enriched wiikite.

The Sc-Yb correlation is explained by the closeness of the ionic radius of scandium to the ionic radii of Yb and Lu, which are the mallest ones among the lanthanides. Scandium is found, however, lso in minerals whose lanthanide maxima fall on Dy and Gd (samarkite and others).

There exists a traditional separation of the rare earths into the erium and the yttrium groups which is accepted in chemistry.

The boundary between these two groups is drawn between Sm and Eu on the basis of solubility differences of the compounds, or between Gd and Tb on the basis of the electronic structures.

The foregoing data on composition of the rare earths in minerals show that the break-down of the series into the cerium and the yttrium groups is entirely inadequate. Indeed, how would one classify the rare earths with the Nd maxima (Nos. 83, 118, 128) or with the Gd maxima (Nos. 41-44, 95, 117)? There is practically no Ce or Y group, the neodymium and the gadolinium respectively. Chemistry knows some rare-earths compositions with the Sm maxima but without any Ce or Y. Depending on positions of the maxima, it is possible accordingly to distinguish five groups of the rare earths: the cerium, the neodymium, the samarium, the gadolinium, the yttrium. The boundary between the gadolinium (or the cerium group by the traditional understanding) and the yttrium groups must be drawn between Tb and Dy. It is not permissible to draw this boundary between Gd and Tb for, were that done, it would mean a rupture of a closest link between an even and an odd element of a couple.

On the basis of their studies of the rare earths in monazite, Murata et al. [3] proposed to divide the cerium earths into two subgroups: the lanthanum (La, Ce, Pr) and the neodymium (Nd, Sm, Gd). In chemistry the yttrium earths are divided commonly into three subgroups: the terbium (Eu, Gd, Tb), the erbium (Dy, Ho, Er, Tm) and the ytterbium (Yb, Lu). This latter classification seems to be irrational, from the mineralogic-geochemical point of view, because it either makes combinations of dissimilar elements or breaks up the closely related even-odd couples. It is more appropriate to divide the groups into subgroups on the basis of the preponderant even elements in the couples. Thus the cerium group may be divided into the following subgroups: the cerium (Ce, La), the neodymium (Nd, Pr), the samarium (Sm, Eu), the gadolinium (Gd, Tb), while the yttrium group may be divided into the dysprosium (Dy, Ho, Y), the erbium (Er, Tm) and the ytterbium (Yb, Lu) subgroups.

It is rational also not to classify separately the cerium and the yttrium groups but to think instead in terms of the primary groups: neodymium, cerium, samarium, gadolinium, dysprosium, erbium, and ytterbium.

The division of the rare earths into the cerium and the yttrium groups is customary in chemical analysis. As shown in Figure 5, however, in the analysis of monazite, the maximum in the so-called yttrium group falls on Gd and not on Y or the yttrium group at all (Dy, Er, Yb).

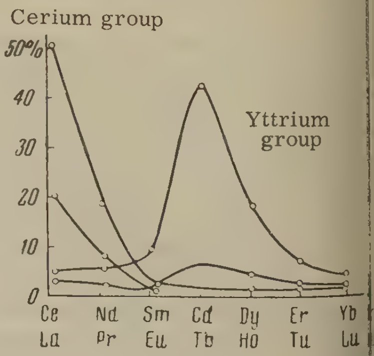

Fig. 5. Composition of rare earths in precipitates of cerium and of yttrium groups of monazite.

This is an illustration of the conventional way of characterization of he rare earths provided by the chemical analysis of minerals. There s no real need to divide the Σ TR_2O_3 into the cerium and the yttrium groups. The color of the precipitate is already a sufficient indication of its qualitative composition. As to the quantitative characterization of the Σ TR_2O_3 precipitate, it is only rational at once to pass it on for ts X-ray spectrographic or the spectrographic analysis.

The dependence of the TR composition on the composition and structure of the minerals is to be reported in our next communication.

REFERENCES

1. Goldschmidt, V. M. and L. Thomassen. Geochemische Verteilungsgesatze, III, *Osl. Akad. Ber.* No. 5, 1924.
2. Borovskii, I. B. and V. I. Gerasimovskii. *Doklady Akad. Nauk SSSR,* 49, No. 5.
3. Murata, K., H. Rose, and M. Carron. Systematic variation of rare earth in monazite. *Geochim. et Cosmochim. Acta.* 4, No. 6, 1953.
4. Murata, K., H. Rose, M. Carron, and J. Glass. Systematic variation of rare earth in cerium-earth minerals. *Geochim. et Cosmochim. Acta* 11, No. 3, 1957.
5. Vainshtein, E. E., A. I. Tugarinov, and N. V. Turanskaya. *Geokhimiya* No. 2 1957.
6. Sahama, T., and V. Vahatalo. The rare earth content of wiikite. *Bull. Com. Geol. Finl.* No. 125, 1939.
7. Wylie, A. W. Lanthanum and scandium distribution in western Australian fergusonite. *Am. Mineral.* 39, 667-669, 1954.
8. Butler, J. Rare earths in yttrotungstite. *Geokhim. et Cosmochim. Acta.* 12, No. 3, 1957.
9. Butler, J. R. Rare earths and thorium in lyndochite. *Am. Mineral.* 42, 671-676, 1957.

0. Hildebrand, F., M. Carron, and H. Rose. Re-examination of Rhabdophane from Salisbury, Conn. *Bull. Geol. Soc. Am.,* Abstr. 68, No. 12, p. 2, 1957.
1. Gerasimovskii, V. I., and N. V. Turanskaya. *Geokhimiya.* No. 4, 1957.
2. Barinskii, R. L. *Doklady Akad. Nauk. SSSR,* 120. No. 3, 1958.

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THE POTASSIUM-RUBIDIUM RATIO IN MINERALS FROM PEGMATITES OF THE KOLA PENINSULA, AS SHOWN BY SPECTROGRAPHIC ANALYSIS

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Abstract

The ratios of the K/Rb content in minerals from pegmatites of the same pegmatite field of the northern part of the Kola Peninsula but showing different mineralogical composition and structure have been studied. It has been ascertained that the K/Rb ratio in microclines varies from 106 in ordinary pegmatitic dikes to 7 in microclines from more complex differentiated pegmatitic dikes. In microclines from zonal pegmatites a decrease of the K/Rb ratio from 26 to 15 has been observed in the direction from the contact to the center. For micas of the pegmatitic field under investigation, an enrichment of rubidium with respect to potassium from NW to S in the field has been observed; in zoned pegmatites the enrichment of micas proceeds from the contact to the core. It also has been noted that the K/Rb ratio in microclines taken from pegmatitic veins belonging to a definite stage of pegmatite formation in similar paragenetic associations remains rather constant and from it is in some degree possible to judge of the mineralogical composition and structure of the pegmatite under investigation. The gradual concentration of rubidium, as well as of other rare elements being especially conspicuous in such minerals as microcline and mica may be explained by the formation of pegmatites of such a type from the residual melt-solution during its gradual differentiation.

The problem of K/Rb ratio in rocks and minerals has attracted the interest of investigators for a long time. These two alkali elements, potassium and rubidium, are intimately bound together geochemically. Their ionic radii (K^+ 1.33 Å and Rb^+ 1.49 Å) and their ionization potentials (K^+ 4.34 v and Rb^+ 4.18 v) are very similar. The difference between their VEK's* is small, being 0.36 and 0.33 for potassium and rubidium, respectively. Rubidium is common in potassium minerals and rocks for this reason, wherein it substitutes for potassium isomorphously.

L. Ahrens and co-workers [1] pointed out, in their studies of the K/Rb ratios in igneous rocks, that the potassium-rubidium association is a very close one and that the K/Rb is practically the same in all principal types of igneous rocks, with the average of 90 (variations rom 55 to 150). Later investigators [2, 3, 4, 5] confirmed the findings of Ahrens, on the whole, but found also that the Rb data of Ahrens are oo high and that his K/Rb ratios are too low accordingly. Their results suggest a K/Rb of about 240 as a more reliable figure for igneous rocks.

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*"VEK", A. E. Fersman's parameter, is energy per unit valence. The energy ("EK") is defined here (in electron-volts or in megacalories) as the contribution per ion to the energy of the unit-cell. VPS

The K/Rb is significantly lower in pegmatites and is at its minimum n minerals characterizing the late replacement stages of complex pegmatites. Thus Ahrens [1] points out that the K/Rb is 6, on the average, in lepidolites, and may be as low as 3. This ratio varies from 21.14 to 5.56 in microclines, according to our calculations based on P. M. Jeffery's data [6]. The lowering of the ratio in pegmatites depends on the accumulation of rubidium, as against potassium, in the end-stages of the pegmatitic process. This accumulation is related to he larger size of rubidium ion [1, 7, 8, 9].

The present study deals with variations in the K/Rb ratio in microclines and micas from pegmatitic veins with different paragenetic associations. All of these veins are situated within the borders of one single pegmatitic field in the north of the Kola Peninsula. A definite regional zoning is noticeable in the distribution of the veins, as expressed in the progressively increasing number of different minerals n the veins, northwest to southeast, and also in the appearance of pegmatitic veins with clearly developed replacement zones in the south and in the southeast of the pegmatitic field here investigated. In the north and the northwest of the field, the veins are composed of microcline, quartz, and of smaller amounts of acid plagioclase and black ourmaline. Zonal veins with intricate structures occur in the east and in the southeast. Microcline, plagioclase, and black tourmaline may be encountered in vicinities of the contacts. In the transitional zone, the microcline crystals increase up to 1 meter in diameter, and smaller amounts of other minerals also make their appearance. The entral parts embrace a zone containing large amounts of minerals esulting from replacements of microcline and of other minerals from ther zones. The replacement zone contains quartz, clevelandite, polucite, tourmaline, rubellite, montebrasite, tantalite, microlite, simponite, stibiotantalite, and other minerals. Microcline is present here in smaller quantities. Detailed descriptions of composition and tructures of these veins were reported in an earlier publication [10].

I. THE K/Rb RATIO IN MICROCLINES

We determined potassium and rubidium in 30 samples of microlines from different pegmatites of the field under investigation. We lso analyzed three samples of microcline from the adjoining pegmaitic field situated to the southeast of the one we had studied and eight amples of amazonites from East Transbaikal and Ural. The latter materials were placed at our disposal by A. S. Pavlenko and A. I. Ginzburg, to whom we are greatly indebted. Potassium and rubidium

Potassium, Rubidium, and K/Rb in Minerals from Pegmatitic Veins, Northern Part of Kola Peninsula

No.	Materials and source	%K	%Rb	K/Rb
	"A". Pegmatitic area in northern part of Kola Peninsula			
	I. NORTHWESTERN SECTION OF THE FIELD			
1.	Microcline from blocky pegmatite, northernmost part of the field	11.17	0.12	93.1
2.	Same place; from graphic-structured pegmatite	10.6	0.10	106
3.	Vein; 14 km SE of No. 2; microcline from blocky part of vein	10.1	0.34	29.7
	"Vein in bog", 4 km E of No. 3			
4.	Pink microcline from zone next to contact with pegmatite	8.06	0.28	28.8
5.	White microcline from intermediate zone	7.95	0.31	25.6
6.	Coarsely crystalline microcline from blocky zone of pegmatite	10.6	0.69	15.4
7.	Microcline from zone of replacement; paragenesis: lepidolite, rubelite, pollucite, cesium beryl	11.65	1.08	10.8
	II. CENTRAL SECTION OF PEGMATITIC FIELD			
8.	Microcline from zone near contact with pegmatite	7.61	0.23	33.1
9.	Microcline from intermediate zone	9.39	0.40	23.5
10.	Coarsely crystalline microcline from zone near contact with pegmatite	12.02	0.55	21.9
11.	Microcline from blocky zone of pegmatite	11.4	0.57	20.1
	III. SOUTHERN AND SOUTHEASTERN SECTION OF THE FIELD			
	(a) Southern veins			
12.	Microcline from marginal zone, vein No. 6	13.74	0.52	26.4
13.	" with grayish-green spodumene	10.2	0.35	29.1
14.	" vein No. 2, 0.2 m. from contact with hanging wall	10.16	0.38	26.7
15.	White microcline, vein No. 2, 3.6 m. from contact with hanging wall.	8.67	0.46	18.9
16.	Pink microcline, vein No. 2, 3.6 m. from contact with hanging wall.	9.99	0.49	20.4
17.	Microcline, vein No. 2, 10 m. from contact with hanging wall	10.14	0.62	16.0
18.	Microcline, vein No. 2, 13 m. from contact with hanging wall	10.71	0.70	15.3
19.	Microcline, vein No. 2, center of vein	10.12	0.55	18.4
20.	Microcline, vein No. 10, center of vein	9.4	0.52	18.1
21.	Microcline, vein No. 10, center of vein	12.83	2.81	4.6
	(b) Vein in the farthest southeastern section of the field			
22.	Pink microcline	9.55	1.05	9.1
23.	White "	12.19	1.55	7.9
24.	" "	9.55	1.05	9.1
25.	" " , creamy tinge	10.26	1.27	8.1
26.	" " , " "	10.09	1.10	9.2
27.	" " , " "	10.85	1.21	9.0
28.	" " , " "	7.84	1.08	7.3
29.	" "	8.95	1.28	7.0
30.	" "	10.48	1.22	8.6

Materials and source	%K	%Rb	K/Rb
(b) Vein in the farthest southeastern section of the field			
Pink microcline	9.55	1.05	9.1
White "	12.19	1.55	7.9
" "	9.55	1.05	9.1
" " , creamy tinge	10.26	1.27	8.1
" " , " "	10.09	1.10	9.2
" " , " "	10.85	1.21	9.0
" " , " "	7.84	1.08	7.3
" "	8.95	1.28	7.0
" "	10.48	1.22	8.6
"B". Pegmatitic field 30 km SE of Field "A"			
Microcline from footwall of vein	8.86	0.30	29.5
" " " " "	9.90	0.33	30.0
" " " " "	8.44	0.37	22.8
"C". Microcline from other districts, Kola Peninsula			
Microcline from porphyry granite from lower course of Panoi River	8.28	0.12	69.0
Biotite, same source as No. 34	4.96	0.12	41.3
Large crystal of microcline, Murmansk area	8.63	0.11	78.4
"D". Pegmatitic fields of Ural and of E. Transbaikal			
Ilmen Mts., Ural; amazonite	9.66	0.29	33.3
Amazonite from pegmatite in granite	10.9	0.30	36.3
Amazonite	10.62	0.46	23.1
Amazonite from amazonite granite	9.06	0.35	25.9
Amazonite from pegmatite in sandy-clayey shale	11.46	0.47	24.3
Zuikilkinda site; amazonite from pegmatite vein	9.78	0.45	21.7
Barukingilda site; amazonite	9.89	0.43	23.0
Etyka, average sample of amazonite granites	3.79	1.20	31.6
"E". Micas (Kola Peninsula)			
Purple lepidolite, large plates, replacement zone in center of vein No. 2	7.71	1.36	5.7
Lepidolite, large plates, replacement zone of vein No. 13	9.00	1.25	7.2
Lilac-brown lepidolite ("Barbot's Eye"); from a vein with a well developed replacement zone	7.26	1.45	5.0
Pale lilac lepidolite; same source as No. 47	6.89	1.90	3.6
Silvery-pink mica	8.19	0.61	13.4
Feathery pink muscovite	7.99	1.02	7.8
Greenish muscovite, vein No. 18, replacement zone	8.36	1.30	6.4
Greenish muscovite, same source as No. 51	7.73	1.58	4.9
Central part of pegmatitic field. Fine scaly muscovite with greenish tinge, vein in center of field	7.49	0.59	12.7

were determined also in coarsely crystalline microcline from the Murmansk area and in microcline and biotite from a porphyry-like granite from the territory along the lower course of the Panoi River.

All of the microclines from the pegmatites of the Kola are microcline-perthites. The perthite in-growths in these microcline-perthite consist of albite and albite-oligoclase, and owe their origin to replacements. Proportions of albite in the microclines are 15 to 20%, as determined by the chemical analysis.

Potassium and rubidium were determined spectrographically, as i our earlier studies [10, 11], in the activated AC arc at 220 v. and 7 amp. A complex carbon electrode was used; the cavity in which the sample was placed was 4 mm deep and 3.5 mm in diameter. The floo of this cavity was lined with 0.025 g of powdered carbon which was tamped down. The sample was placed on this floor and was covered by a thin layer of powdered carbon. The spectra were photographed i the ISP-51 spectrograph using a camera with 270 mm focus. The image of the source was projected on the slit of the spectrograph by means of two lenses, one of which was equipped with a moveable diaphragm. Width of the slit was 0.02 mm; height of the interposed diaphragm—3.2 mm. A two-stage reducer was placed in front of the slit, capable of reducing intensity of the spectrum 3-fold in the second stage. The exposure was 5 minutes.

Rubidium content was determined by two lines: 7800.23 and 7947.60 Å. Potassium was determined in the same spectrograms by the lines 7664.91, 7698.98 Å and 6911.30, 6938.98 Å. The rubidium lines and two of the potassium lines, 7664.91 and 7698.98 Å, were recorded on the Infrakhrom 840 and were photographed on the Infrakhrom 760 film Sections of these films were inserted simultaneously inside the cassette, in their appropriate places. The nomograms were constructed with the log c and the ΔS coordinates, where "c" is the concentration of the element sought and ΔS is the difference between density of the background (next to the line) and the density of the line of the element (Figs. 1 and 2). These nomograms are straight lines within the following limits of the concentrations: 5×10^{-2} to 7×10^{-1}% for Rb; 3.5 to 10% and 1.3 to 10.5% for potassium, for lines 6911.3, 6938.98 Å and 7698.98, 7664.91 Å respectively. Densities of Rb lines 7800.23, 7947.60 and K lines 6911.3, 6938.98 Å were measured in the original spectrum without the reducer. The reduced part of the spectrum was used in measuring densities of the K lines 7698.98, 7664.91 Å. The background of the spectrogram was measured always in the original spectrum. Relative errors of the analyses, as shown by replicate measurements, were ± 8% for Rb and ± 7.4% and ± 9.4% for K, lines 6911.3, 6938.98 Å and 7698.98, 7664.91 Å respectively. Most of the determinations of K were done by means of lines 6911.3 and 6938.98 Å; lines 7698.98 and 7644.91 Å were used only when the samples were diluted 3-fold with albite, as in the analysis of muscovites, lepidolites, and rubidium-rich microclines.

Standards were prepared from icrocline in which K and Rb ere determined previously by e flame photometer. This icrocline was diluted with bidium-free albite containing own amounts of potassium, in der to obtain the desired se- ence of lower concentrations.

The results are presented in e table.

The results are interpreted follows:

1. Potassium is 7.84 to .74% and rubidium is 0.1 to 5% in microclines from peg- atitic veins of different com- sition.

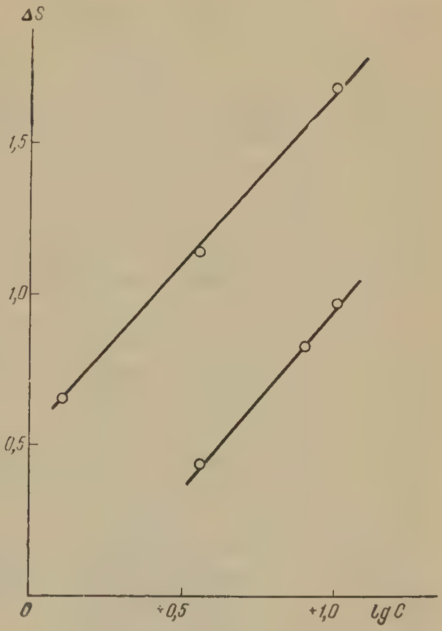


Fig. 1. Nomograms for determination of rubidium in microcline by the line 7800.23 Å.

2. The K/Rb ratio varies om 106, in microclines from gmatitic veins in the north d northwest parts of the peg- atitic field, to 7.0 in micro- nes from pegmatitic veins the southeast part of the ld. If we plot the Rb content on the abscissa and the K/Rb on the dinate of a diagram (Fig. 3), four areas may be recognized, as was ind for the Rb/Cs ratio, in an earlier publication.

Area I; K/Rb = 36 to 106; the highest one of all; microclines from northern and the northwestern sections of our pegmatitic area, the crocline and the biotite from the porphyry granite along the lower noi, and the coarsely crystalline white microcline from the rmansk area.

Area II; K/Rb = 23 to 36; microclines from the border zone in the thwestern part of our area, the microcline from the neighboring gmatitic area, and amazonite specimens from the pegmatitic veins Ural and Transbaikal.

Area III; K/Rb = 15 to 23; microclines from the blocky and inter- diate zones of the zoned pegmatites and microclines from the re- cement units of the southern and southeastern veins.

Area IV; K/Rb = 4.6 to 15; microclines from pegmatitic veins in ich the replacement units are extensively developed.

3. The K/Rb ratio in microclines from the eastern and southeastern tions of our area decreases from the border toward the core, as m 26 to 15 (Fig. 4).

Thus we observe a relative enrichment of rubidium on transition m the earlier and simpler pegmatites to the later ones, i.e., the complex, differentiated, and the rare metal-rich pegmatites, in harmony with the theoretical deductions regarding the accumulation of rubidium in the end-stages of the process of pegmatization [1, 3, 4, 5, 6, 7, 8, 9]. Progressive and gradual enrichments of this kind, in the pegmatization, is observed also for a whole series of other rare elements, such as Li, Cs, Ta, [10, 11]. It has been also noted that the K/Rb ratio in microclines from pegmatitic veins which belong to certain definite stages of the pegmatization process and involve paragenetic associations of the same kind, remains fairly constant, thus enabling us to form an opinion regarding mineralogic composition and structures of the pegmatite in question.

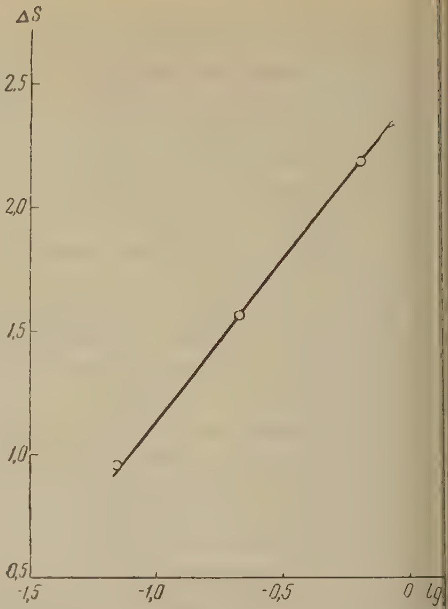


Fig. 2. Nomograms for determinatio of potassium by the lines 6938.98 and 7698.98 Å (II).

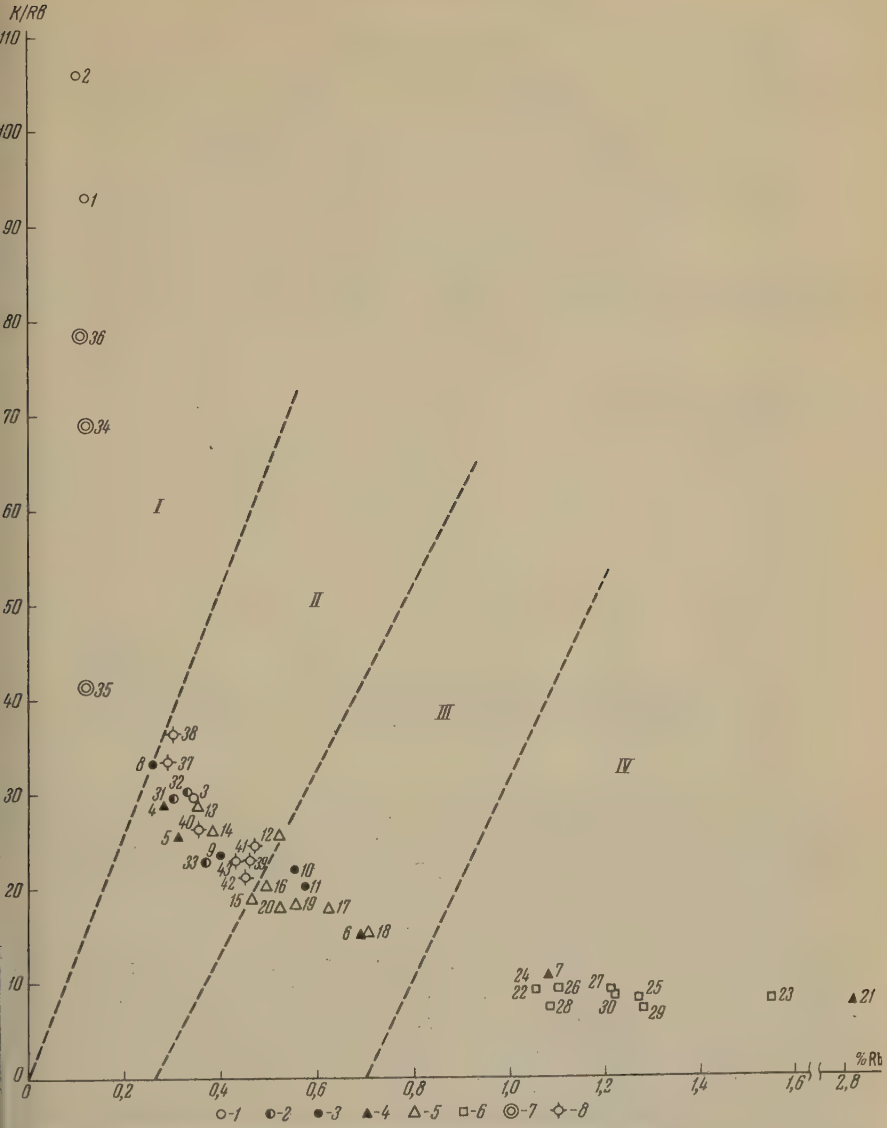
II. THE K/Rb RATIO IN MICAS

We determined the K/Rb ratio in 9 samples of mica. The determinations were quantitative-spectrographic, like the analyses of microcline The results are reported at the end of the table. There are several ge erations of muscovite and lepidolite in the pegmatitic dikes of the Kola Peninsula.

The following generations and varieties of muscovite are found: (a) muscovite in large sheets, generations I and II; (b) fine-scaly muscovite; (c) cryptocrystalline muscovite; (d) pink muscovite; (e) pale pink muscovite, grading into greenish.

We determined potassium and rubidium in: two specimens of the sheet muscovite II, the later generation (analyses Nos. 51, 52 in the ta ble) which is accompanied by minerals typical of the replacement zon the fine-scaly muscovite from a dike in the central section of the pegmatitic field (analysis No. 53 in the table); cryptocrystalline muscovit pink feathery muscovite (analysis No. 50). The results show that the K/Rb ratio decreases also in muscovite on transition from the pegmatitic dike in the center of the field, where this ratio is 1.27, to the pegmatic dike in the southeastern section of the field where the replacemen units are developed extensively and where the K/Rb ratio is 4.9 to 6.4.

Lepidolites are found chiefly in the southeastern dikes of the field, in paragenetic associations typical of replacement units.



ig. 3. Diagrams of Rb contents and K/Rb ratios in microclines from different
egmatitic veins: 1-microcline from pegmatitic dikes, NW section of pegmatitic
eld, northern part of Kola Peninsula; 2-microcline from pegmatitic dikes in a
eighboring field; 3-microcline from pegmatitic dikes, central part of the peg-
atitic field under the present investigation; 4-microcline from the "bog" peg-
atite dike; 5-microcline from zoned pegmatite dike of the southeast of the
rthern part of the Kola Peninsula; 6-microcline from pegmatite dike in the
utheast of the pegmatitic field with a strongly developed replacement unit;
-microcline and biotite from granite in the area along the lower course of
noi River and coarsely crystalline microcline from Murmansk area; 8-ama-
nites from Transbaikal and Ural. Figures at symbols in the diagram refer
item Nos. of Table 1.

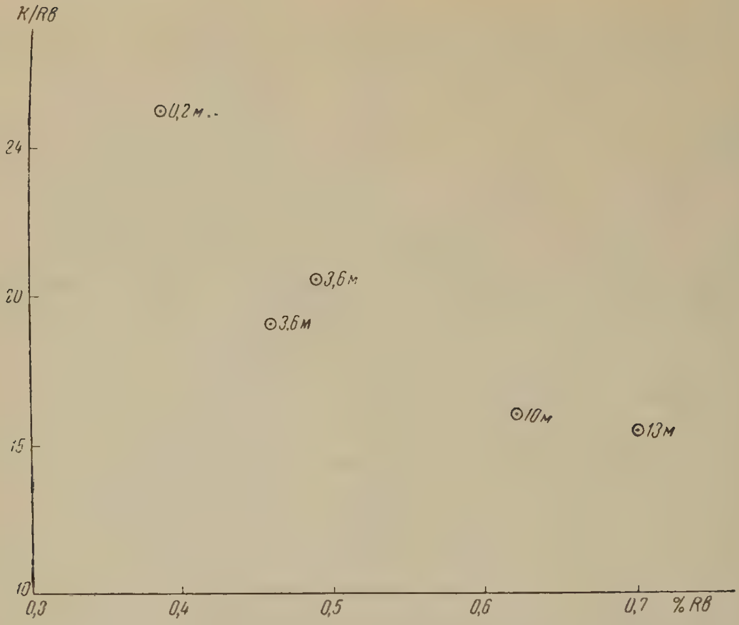


Fig. 4. Relationship between Rb and K/Rb in microclines from pegmatitic vein No. 2. Figures in the diagram are distances from the vein's contact.

The lilac-colored lepidolite from a vein with a strongly developed placement zone has the lowest K/Rb ratio, 3.6 to 5.0 (analyses Nos. 4 47 in the table); this ratio is 5.7 to 7.2 in the purplish lepidolites (ana yses Nos. 45, 46 in the table).

There is a tendency accordingly toward a relative enrichment of rubidium in micas, as well as in microclines, from the northwest to t southeast of the pegmatitic field, whereas, in the zoned dikes, rubidiu is enriched in micas from the contact toward the core of the dike.

The general tendency toward a gradual accumulation of the rare elements in pegmatites is particularly well exemplified in minerals like microclines and micas. In our opinion, this is explained by the formation of the pegmatites, which are so enriched from the residual solution-melt, as the result of gradual differentiation.

In conclusion, the authors wish to thank Academician A. P. Vinogradov for his valuable suggestions and guidance in this research, as well as V. I. Gerasimovskii and E. E. Vainshtein for their cooperation in the present study.

REFERENCES

1. Ahrens, L. H., W. H. Pinson, and Margaret M. Klarus: *Geochim et Cosmochim. Acta,* 2, 229, 1952.

2. Smales, A. A.: *Geochim. et Cosmochim. Acta*, 8, 300, 1955.

3. Herzog, L. F., and W. H. Pinson: *Geochim. et Cosmochim.* Acta, 8, 295, 1955.

4. Nockolds, S. R., and R. Allen: *Geochim. et Cosmochim. Acta*, 4, 105, 1953.

5. Taylor, S. R., C. H. Emelens, and C. S. Edley: *Geochim. et Cosmochim. Acta*, 10, 224, 1956.

6. Jeffery, P. M.: *Geochim. et Cosmochim. Acta*, 10, 191, 1956.

7. Fersman, A. E.: *Pegmatity* (Pegmatites). *Izd. Akad. Nauk. SSSR*, Moscow, 1940.

8. Ginzburg. A. I.: *Trudy Mineralogicheskogo Museya.*

9. Ahrens, L. H.: *Geochim. et Cosmochim. Acta*, 3, 1, 1953.

0. Borovik-Romanova, T. F., and A. F. Sosedko: *Geokhimiya*, No. 5, 368, 1957.

1. Borovik-Romanova, T. F., and E. D. Kalita: *Geokhimiya*, No. 2, (*Geochemistry* No. 2, pp. 141-150) 1958.

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GEOCHEMICAL ZONATIONS IN THE BLYAVA DEPOSIT ON THE WESTERN SLOPE OF THE SOUTHERN URALS

(In Relation to Migration of Elements in the Oxidized Zone and to Development of the Weathered Crust)

L. D. Herman

Abstract

The behavior of a number of chemical elements in the zone of oxidation, so
fixation forms of these elements, and their distribution in the ore body and in t
host rocks are considered. Separate groups of elements with similar behavior
have been fixed. A definite trend in the migration processes of elements towar
dissemination of ore components into the host rocks and separation of individua
elements at certain distances from the ore bodies has been determined. A sup
gene zonation has been ascertained for a number of chemical elements around
the ore bodies and ore fields, both horizontal and vertical. The enriched zones
either co-exist or overlap one another. Geologists may use the studied sequen
in the distribution of elements among supergene altered rocks as well as the
mineral composition of zones for interpretations of new areas. The mineral-
ogical-geochemical investigation gives to the prospecting geologist a rather pr
cise idea of the location and depth of the ore-body occurrences and of their com
position.

The Blyava chalcopyrite deposit is best suited for studies of the supergene alteration of its host rocks, from the mineralogic-geochem ical point of view, out of all other known deposits of this kind in the greenstone belt of the Urals. This deposit was already studied in some detail [8, 9, 10], etc., was fully explored, was exposed to 100 meters depth by mine workings, was exposed at the surface by an ope cut, and was already mined out to a large extent.

This object of our study has a particular merit, namely, the immense span of the supergene processes over a wide range of geologic time, after the emergence of the main ore body, the Northern Lens, a the surface, that is, from Triassic to modern times. Supergene alterations reach 350 to 400 m. depths in the ore body itself and 100 to 200 m. depths in the host rocks. It becomes possible, therefore, to observe the end stages of the migration and fixation of substance in the upper horizons of the deposit while observing their earliest stages in the deepest horizons.

Moreover, both in the mine workings and in the open cut, there was an opportunity to collect materials characteristic of the modern migration of chemical elements in the oxidized zone (mine waters, modern incrustations, efflorescences, rocks and ores altered by saline weathering, etc.).

The author's aim in the present study was to put to use all of the remendous body of field data and observations accumulated by mining eologists and explorers, as well as his own long working experience bout 15 years) in the Blyava District.*

As a result, we arrived at certain relationships in the distribution f elements in the host rocks, during supergene processes, whereby e consequent mineralogic-geochemical zonation in rocks surrounding e Blyava deposits was made manifest. Let us consider only certain eneralized findings in our studies, within the scope of the present ort article.

GEOLOGIC ENVIRONMENT

Like other pyritic deposits of the Urals, the Blyava is situated mong the rocks of the spilite-keratophyre formation [A. N. avaritskii, 4], in the confines of the greenstone belt. The largest re bodies are associated with contacts of the larger keratophyre-pilite massifs and areas abounding in tuffs and tuff-breccias which re tectonically the most weakened areas. There is no excluding the ossibility that tectonics played a major part in localizing the ore odies. The ore bodies are conformable with their host rocks as a le. They dip at 70 to 80° to the west or the southwest in their upper orizons, but only at 45 to 20° in their lower horizons, which is an in-cation of a flattening-out of the ore bodies in depth.

A genetic relationship of the ore bodies to the intrusives (quartz eratophyres) is still controversial, although from the practical point view the assumption of such relationship is useful in prospecting, nce no economic mineralization could be proved so far in the ab-ence of the quartz keratophyres.

A weathered crust, not more than 30 to 40 m. below the level of the re-Jurassic peneplane, was found during prospecting and exploration. his weathered crust sinks to greater depths at contacts with the ore odies, where its conspicuous expression is in fragmentation and in egradation of the rocks to the clayey state. There is a clearly de-ned vertical zonation and a well developed oxidized zone in ore bodies tcropping at the surface. The structure of the oxidized part of the rgest ore body, the Northern Lens, is characterized by a downward quence of the following sub-zones:

a) The subzone of iron oxides and hydroxides represented by hydro-matite, hematite, goethite, and hydrogoethite, with subordinate quan-ies of jarosite, quartz, gypsum, and barite.

pectrographic, chemical, dithizone, optical, thermal, X-ray, electronic, minescent, isotopic, and other examinations of his materials were performed the author at the Institute of Geology of Ore Deposits, Petrography, Min-ralogy and Geochemistry, Academy of Sciences of the USSR, under the direc-on of I.I. Ginzburg.

b) The subzone of jarosite, with a small quantity of opal, quartz, and gypsum.

c) The subzone of a loose flint-gypsum material consisting of gypsum, opal, quartz, native sulfur, barite, anglesite, jarosite, destinezite and more rarely, pyrite, iron hydroxides, silver halides, phosphoscorodite, and other minerals.

d) Interlayers of covellite and native sulfur between subzones c) and e).

e) Inclusions and veinlets of cuprite and native copper in host rocks coinciding hypsometrically with the interlayer of covellite and native sulfur above the ore body; extensive development of gypsum veinlets, tenorite, red and black copper ores, magnetite, martite, etc.

f) The subzone of a pyritic loose material and of porous pyritic ore with local clusters and "nests" of native sulfur and covellite.

g) The subzone of sulfide ores with large amounts of secondary sulfates and sulfides. An abundance of secondary supergene iron bysulfides and of complex sulfates, especially at contacts with the rocks (slavikite, copper copiapite, pickeringite, halotrichite, alum, and many others).

Not only the ore bodies but also the host rocks were subjected to a highly active and prolonged chemical re-working in the course of the long and involved history of alteration and transformations of minerals composing the pyritic ore. As a result, the broad zones of altered rocks, so conspicuous in the field, made their appearance. However, it was generally difficult to discover the closely confined ore bodies within the broad bands of altered rocks and, for that reason, mineralogic-geochemical studies of these bands was found to be definitely useful.

MIGRATION OF ELEMENTS AND GEOCHEMICAL ZONATIONS

Some chemical elements resemble each other in their behavior both in their modern and in their ancient migrations, wherein they develop clearly defined enrichment zones, and such elements may be grouped accordingly under the following categories:

I. The principal chalcophilic elements: Cu, Zn, S, Fe (as sulfides).

II. The chalcophilic accessory elements: Ag, Au, Pb, As, Mo, Co; the behavior of Ca and Ba is analogous in the migrations.

III. Lithophilic elements. These elements fall definitely into two subgroups:

a) Ca, Mn, Mo, Fe (in rocks), Si, V.

b) Mg, Al, Ti, Ni, Co (in rocks) act, in many instances, as if they were transitional to the chalcophile group. Mg and Zn especially resemble each other, both in their migration and in the formation of enrichment zones at 100 m. depths below the surface, as they appear in conjugate fixed forms in efflorescences (epsomitegoslarite). At shallower depths (68 to 75 m.) they are joined by iron-maghemite-siderite.

IV. Others. All rare and dispersed elements are referred to this roup. Here, also, two subgroups may be clearly distinguished.

a) Elements whose role is insignificant or obscure, whose manner of fixation, as minerals of the oxidized zone, has been neither studied nor ascertained: Sc, Sr, Zr, Cr, Ni, Cl, Br, I. P also belongs to this subgroup; although, for some local reason at the Blyava, P is sufficiently abundant in the oxidized zone to form thick (12 in.) accumulations of destinezite [Herman, 3], its role is not entirely clear.

b) Elements accompanying the ore bodies: In, Sn, Bi, Cd, Sb, Co, Se, Te, Ge, Be. As a rule, these elements have a very limited mobility and they are not subject to a far-flung dispersion in the host rocks; they are fixed in minerals within a few tens of meters from the ore body. Their value in geochemical prospecting for pyrite deposits is considerable, for that reason. Germanium and beryllium are not characteristic of the Blyava, however, and are found but rarely in the district.

Let us consider now in brief the characteristics of the groups here numerated.

The Principal Chalcophilic Elements

S, Fe, Cu, Zn, the main constituents of the ore body, belong to this roup.

The common and essential features of these elements are as folws: a) their abundance in the ore body or in some of its parts; their tendency toward dispersion in the surrounding rocks in oxizing environments; c) their repeated solution, redeposition, and igration within the ore body and especially outside its boundaries; their capacity to form easily soluble compounds and to be precipited from solutions.

Sulfur of the sulfides, in supergene processes, undergoes succesvely all stages of the oxidation, from the sulfide to the elemental lfur, and on to the sulfate: $S^{2-} \rightarrow (S_2)^{2-} \rightarrow S^0 \rightarrow S^{4+} \rightarrow S^{6+}$. There is so a redistribution of sulfur in the ore body, related to its enrichent in the upper part of the leached zone, as well as in the hanging ll of the ore body within the leached and the cementation zones. condary bisulfides of iron and native sulfur are so derived. Moreer, there is no excluding the possibility that thiosalts of iron play a ajor part in the redistribution of sulfur—the derivates of thioarsenic id, which is the strongest oxidizing agent in oxygen-deficient enronments (sulfur takes on the function of oxygen in thio acids). It is obably for this reason that supergene iron bisulfides contain from ths of one per cent to several per cent of arsenic. There is a fortion of unstable S^{4+} compounds, as indicated by the accumulations the sulfurous gas in mine workings. And, finally, the abundance and the effects of S^{6+} compounds are immense. The abundance of sulfate in the ores and in the host rocks, the easy solubility of these compounds in natural waters, and the presence of appreciable quantities free sulfuric acid (up to 88.2 g/liter, and more), conducive to solutio of most of the compounds originating in the oxidized zone, all these factors serve to explain the active migration of sulfur beyond the ore body boundaries and its dispersion in the host rocks. In the footwall rocks, the movement of sulfur as SO_4^{2-} extends farther than 100 m. away from the ore (it was not studied in detail beyond this range). In the hanging wall, the migration of sulfur falls off at 50 m. distance from the ore, because of the neutralization of ore acid waters by carbonate veinlets and by amygdaloids in the diabase. The host rocks ar disingrated by the sulfur-bearing acid waters and are converted into monothermite,* hydromica, kaolinite, or halloysite clays. Thus tremendous quantities of iron and aluminum sulfates, as well as of alkalies, are laid down, forming strong enrichment zones of jarosite and opal-jarosite in the rocks of the hanging wall (basic rocks) and of aluminite and alunite in the footwall (acid rocks). Idealized positions of sulfur-rich and iron-rich zones are shown in Figure 1.

Iron is active in the migration processes and, together with sulfur forms the bulk of the salts in the mine waters on which their mineralization depends. The migration of iron is particularly intensive in the zone of secondary enrichment and in the leached zone where sulfates of iron and others are formed from sulfides. The redistribution of this substance within the ore body is analogous to the redistribution of sulfur. There is a formation of

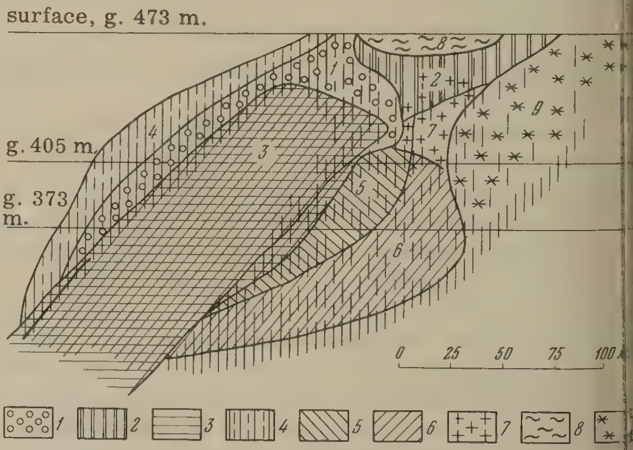

Fig. 1. Zones enriched by sulfur and iron: 1-iron-oxid sulfate zone (jarosite); 2-oxide-iron zone (iron gossan) 3-sulfate-sulfide zone enriched by sulfur and ferrous i 4-sulfate-calcium zone; 5-sulfate-zinc-magnesium-aluminum zone; 6-sulfate-ferrous iron zone; 7-sulfate-aluminum-calcium zone; 8-flint-gypsum loose material 9-deposition of iron in fissures.

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*"Monothermite" is discredited outside the USSR; it is probably a fine-graine mixture of kaolinite and hydromica or "illite." T.S.L.

secondary iron bisulfides which may be precipitated, in places, even after the precipitation of supergene sulfates which is an indication of local reducing environments. The secondary character of such iron bisulfide was established not only by polished section studies but also by the isotopic composition of the sulfur in the specimens [Vinogradov, 2], as well as by measurements of the thermoelectrodynamic capacity of the crystals by means of the "pyritic geothermometer".

Together with the active departure of sulfate iron outside the boundaries of the ore body, there is just as active removal of iron from the host rocks near the contact with the ore. The corresponding iron-enrichment zones are asymmetric with respect to the ore body (Fig. 1). They are practically next to the contact, in the hanging wall (the opal-alunite zones), alongside the ores, together with silicon and sodium, whereas in the footwall there develops a certain differentiation of the substance: ironstones and ferruginized rocks are formed in the oxidized zone (in the part next to the surface); farther down, the rocks become enriched by iron sulfates; still deeper, in the zone of cementation, supergene iron bisulfides are formed from sulfate solutions. The reduction of the sulfated solution, with the resulting formation of iron bisulfides, is especially intensive in the tuffs of the footwall, which had been decomposed into monothermite clays. The near-contact zone, enriched by the secondary iron bisulfides, is not extensive. This zone may be regarded more plausibly as a "smear halo" of the ore body itself to which the vagueness of the eastern contact of the ore body with the surrounding rocks may be attributed. In addition, there is another iron-enrichment zone, 90 to 100 m. from the ore body, which is expressed in abundant adhesions of iron oxides in fissures of the bleached and leached keratophyres near the surface and by iron sulfates, as well as by the secondary pyritization of the rocks at 100 m. below the surface (the iron-enrichment zone, in this latter case,** is closer to the ore body, i.e., is about 70 to 80 m. away from the ore).

Copper is leached out almost entirely both from the oxidized and the leached zones. An accumulation of copper in the ore body is observed only in the zone of secondary enrichment, especially in the footwall, where its content is 1.5 to 2 times as high as in the primary ore, up to the maximum of 30%, in places. Quantitative aspects of the migration of copper are as follows, as, for example, in the case of the northern Lens of the Blyava: In 1941, by a cementing installation at the mine, 20% copper, as of the total exposed reserves of copper, was extracted from dilute waters of the mine. Comparisons of average

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The isotopic composition of sulfur in the supergene and hypogene pyrites of the Blyava was determined by M.S. Chupakhin and V.A. Grinenko at the V.I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR. Measurements of the thermoelectrodynamic capacity of the crystals were performed by V.P. Loginov (IGEM, AN USSR).

That is, the distance from the ore to the enrichment zone decreases somewhat with depth. VPS copper content of ore blocks and layers, as determined 10 to 15 years apart, indicates an average removal of 23% of total copper in the ore during this time interval.

Sulfate is the principal carrier of copper in its migration, and ther is a definite relationship between the copper content of mine waters a their pH, as well as the general character of their mineralization (co per "highs" correspond to the most acid waters).

The migration paths of copper pass not only through the ore bodies but through the host rocks as well, where copper minerals (native co per, cuprite, tenorite, atacamite, malachite, azurite, etc.) form the zone of supergene enrichment. This zone extends 10 to 100 m. away from the ore body (Fig. 2) and contains practically no sulfides, while enveloping the massive and the disseminated ore bodies of pyrite and indicating their boundaries. Such zones were observed by us on the periphery of the Blyava ore field, at the Komsomolskii, and Razumov skii deposits. The fact that such zones are supergene is proved by th presence of cuprite and native copper inclusions in diabases of the hanging wall of the Intermediate Lens, as exposed by an exploratory cross-cut at 100 m. depth below the surface. This Lens is a sunken northern section of the Southern Lens. For this reason, its oxidized zone (the ironstones) is found at 100 m. below the surface and its cuprite and native copper enrichment zone is in the same place as in the Northern Lens, in respect to the vertical zonation. Moreover, the supergene origin of the copper-enriched zones is indicated by the forms in which cuprite, native copper, azurite, malachite, tenorite, atacamite, etc. were separated in fissures and veinlets, by their

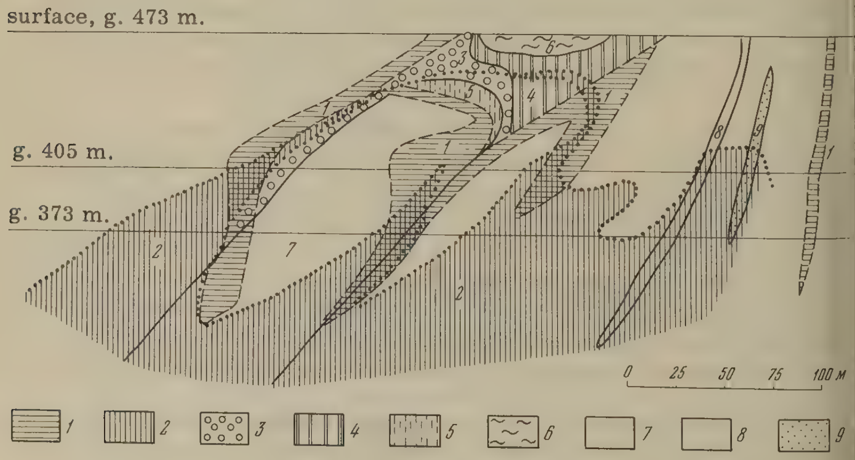

Fig. 2. Zones of enrichment by copper and zinc: 1-copper enrichment zone 2-zinc enrichment zone; 3-iron oxide-sulfate zone (jarosite); 4-iron oxide zone (gossan); 5-flint-gypsum loose material; 6-precipitated sediments; 7-boundaries of ore body; 8-boundaries of the small lens; 9-lens No. 1.

aragenesis with gypsum, magnetite, martite, and other iron oxides, nd by the positions of these zones in the profile.

Zinc is one of the principal economic constituents of the deeper res of the Northern Lens. Zinc is practically gone from the upper orizons of the ore body. Because of its tremendous migration capac- y, zinc is carried out intensively outside the ore-body boundaries into ie host rocks, where it may be retained to some extent, however, in ertain clay minerals and iron hydroxides, as zinc carbonate in the ontact zones and in the upper horizons of the oxidized zone—an indica- on of the former presence of zinc in the pyritic ores themselves. races of zinc remain in the host rocks, as the minerals here enumer- ed, forming relatively zinc-rich zones in these rocks. Such zones e much broader than zones of the other minerals, especially at 100 m. low the surface and at greater depths. They coincide, in space, with e zones of enrichment by iron, aluminum, copper, and manganese, hich is an indication of the wide pH range wherein the precipitation of nc is possible. The enrichment of zinc in the rocks of the hanging all and in the ironstones is due to the carbonates. In the rocks of the otwall, on the contrary, zinc is rarely found.

A part of the ore body outcropping directly at the surface proves to practically zinc-free, whereas another part of the ore body, under e overburden protecting it from the descending surficial waters, oves to be enriched in zinc. This small part of the preserved ores stifies to the colossal scale of the migration of zinc outward from the e body and to its dispersion in surrounding rocks.

Positions of the zones enriched by the elements of Group 1 are own in Figures 1 and 2. These diagrams are profiles through the per part of the Northern Lens ore body, to the depth of 150 to 200 eters. The profiles pass roughly through the center of the Lens, uthwest to northeast, and across the extent of the ore body. The en- chment zones of individual elements, indicated by different shadings, e shown conventionally and to scale, in the diagrams. Diagrams for ner elements in the Group are constructed analogously. It must be ken into account that there are variations in the mineral composition, respect to this or that element, depending on the depth as well as on horizon, constituting its own mineralogic zonations, which are re- ed, in turn, to variations in the physicochemical environments of the gins and of the existence of the minerals in question.

In the instance of copper, for example, the enrichment of the ore dy to 100 m. depth is due chiefly to covellite and copper sulfate but due to chalcocite at greater depths. Rocks of the hanging wall—to m. depth—are enriched by cuprite and native copper, but by copper fate at greater depths. The enrichment of the footwall rocks is due enorite, azurite, malachite, down to 20 m. depth and, at greater ths, to copper sulfates, covellite, and, finally, chalcocite. Cuprite native copper are in the enrichment zones at some distance from Northern Lens. The mineral forms of the fixation of iron and sulfur indicated diagrammatically in Figure 1.

Thus the principal elements of which the ore body is composed, tending to a dispersion in the surrounding rocks, during supergene processes, form perfectly well defined geochemical zones. This zo tion is expressed as a series of successive zones, each of which is enriched by some principal mineral containing the principal elemen of which the ore body is composed. The zones so enriched by this o that mineral or element may overlap each other which indicates changes in their physico-chemical environments (e.g., the impregna with gypsum has its beginnings in the ore body itself but comes to a end in the host rocks locally up to 100 m. away from the ore body, a farther.

II. Chalcophilic Accessory Elements

Ag, Au, Pb, As, Mo, related genetically to the ore body but prese only in small quantities in the ore body, are classified as the chalco philic accessories. They resemble each other in their migrations i the supergene environments. Barium and gallium also belong to thi group.

A limited migration capacity is characteristic of the elements he enumerated, as well as their capacity to form enrichment zones chi at the contacts between the ore and the rocks. True, it is only rarel that we may observe fixation of these elements in their stable forms their enrichment is chiefly neomorphic (as "sweat",[†] efflorescence,[‡] in mine waters, etc.) which is an indication of their cont ing and intensive migration away from the ore body. There is a sub stantial enrichment of these elements in the neomorphs in the contac zone of the Northern Lens footwall at 100 m. below the surface; alre at the 68 to 76 m. depths, the enrichment is confined to veinlets in th rock.[**] This fact is an indication that migration of the elements here enumerated is continuing at 100 m. but is coming to a standstil 68 to 76 m. below the surface. Figures 3 and 4 show that the enrichment zones of the accessory elements, in the ore body and in the hos rocks, do not extend farther than ten meters from the contact zone. measure of their enrichment in the hanging wall, as far as 20 to 60 from the ore, is due probably to the proximity of the Western Lens situated in the rocks of the hanging wall. A comparison of the amou of these elements present in mine waters with their amounts in the corresponding neomorphs ("sweat", efflorescence, veinlets) shows t the maximum amounts of these elements in mine waters go side-by-side, more often than not, with their absence in the neomorphs.

Lead (as galena and in barite) amounts to hundredths of one per c in the primary ores. The lead content becomes irregular nearer the

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[*] As veinlets in the altered parts of the rock.

[†] The "sweat" is liquid gel-like neomorphs.

[‡] The efflorescence is neomorphs crystallized at the surfaces of mine workings.

[**] In the original "veinlets and rocks"; possibly a misprint, judging by the context and by the diagrams. VPS.

surface and the bulk of lead becomes displaced toward the footwall. Enrichment of the footwall by anglesite ($PbSO_4$), alongside covellite, chalcocite, iron sulfates and bisulfides, may be so appreciable in places that the lead content of some of its parts may be up to 7 or 10%. The flint-gypsum loose materials, the interlayers of native sulfur and covellite, as well as the host rock contacts, are also nriched by anglesite (Fig. 3).

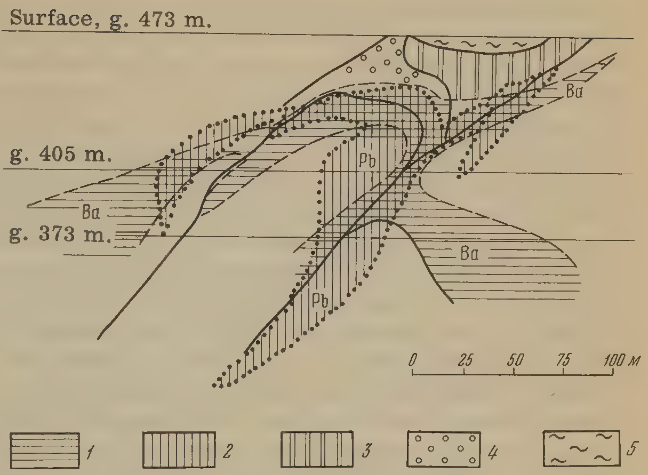

Fig. 3. Zones of enrichment by barium and lead: 1-barium enrichment zone; 2-lead enrichment zone; 3-iron oxide zone (gossan); 4-iron oxide-sulfate zone (jarosite); 5-precipitated sediments.

The migration of lead is continuous, as is shown by the presence of everal generations of anglesite differing among themselves not only in egard to the time of their formation but also in their form and in the ize of their crystals. We have examples where the lead content of ine water exceeded the solubility of lead sulfate in distilled water bout 100 mg/liter as against 42 mg/liter). It is believed that a part the lead in mine waters is present as lead chloride. The migration lead into the host rocks is generally confined to the distance of less an 10 m. but as an exception may be up to 20 m.

Barium may be as high as 2.5% in the zone of the sulfide ores. here is a tendency toward enrichment of barium in the ores of the nging wall in the zone of the secondary sulfide-sulfate enrichment. e flint-gypsum loose material, the ironstones of the central part of e Northern Lens, and the keratophyres of its footwall are also enched with barium. The maximum of the migration of barium outward om the ore body is taking place at this time chiefly into the host rocks the footwall. Figure 3 shows that the barium and the lead enrichment nes coincide more or less only in the upper horizons and that, at 100 below the surface, barium migrates farther than lead and produces ich broader enrichment zones. Moreover, barium acts entirely difently from strontium in supergene environments, and strontium tent of the barium-enriched zones is invariably at its minimum. rium is fixed as barite in the enrichment zones.

Arsenic amounts to hundredths of one per cent in the deeper horizons of the ore body. Its content is somewhat higher in the zone of cementation and is 2 to 3 times as high in the tops of the zone of secondary enrichment, which makes the ore unsuitable for beneficiation. From 100 to 200 m. H_3AsO_4 per liter is present invariably in mine waters [Khitarov, 11]. Supergene iron bisulfides are especially enriched with arsenic (up to several per cent). Such enrichment of the products of the chemical reactions within the iron and the sulfur cycles, in the course of the development of the oxidized zone, by arsenic may be related probably to the formation of salts of iron and of thio-acids* of arsenic yielding sulfides of arsenic and iron on their decomposition. Native sulfur, also arsenic-enriched, was forming in the upper zones, where the access of oxygen was facilitated, along with the iron bisulfides. There was a time of the "brief" existence of arsenic in solution and of a limited migration of arsenic into the host rocks at pH 2 to 3, as well as a precipitation of arsenic from the mine waters already at pH 3 to 5.2. Consequently, the arsenic enrichment zones in the host rocks do not extend farther than 8 to 10 m. from their contacts with the ore body.

Silver and *Gold* are present in the primary ores, in amounts comm for pyrites (tens of grams of Ag per ton and up to several grams of A per ton, with the Au:Ag = 1:15 to 20). There is an appreciable body of literature on migrations of silver and gold in the oxidized zone of the Blyava [Shadlun, 10; Kreiter, 6; Rogover, 9] and we shall not consider

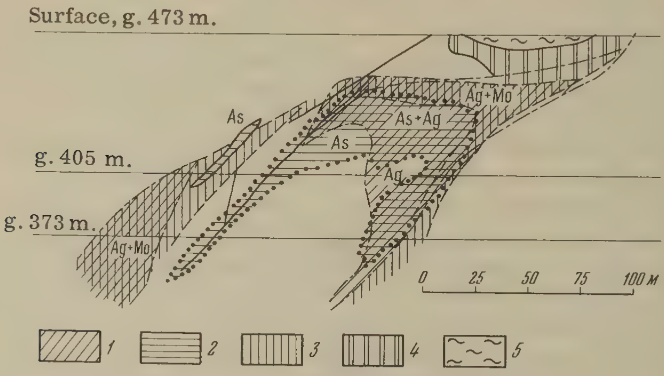

Fig. 4. Zones of enrichment by arsenic, molybdenum, and silver: 1-silver enrichment zone; 2-arsenic enrichment zone; 3-molybdenum enrichment zone; 4-iron oxide-sulfate zone (gossan); 5-precipitated sediments.

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*Stable only within a narrow range of acid pH [Nekrasov, 7].

t here. We should point out only that the greatest accumulation of noble metals is observed in the flint-gypsum loose material in which he Au:Ag ratio is 1:7 to 10, i.e., much higher than in the ore, indicative of the difference in the behavior of gold and silver in supergene processes and of departure of a certain amount of silver. According to A. Brodskii [1], the ground waters of Blyava appearing at the surface contain traces of silver at distances up to 100 m., and farther, from the ore body. Nevertheless, the silver enrichment zones were observed by us only at the contacts of the ore bodies and in very narrow bands over the ore (Fig. 4). We are justified in suggesting that arsenic plays a role in accelerating the migration of gold, on consideration of the gold-gypsum-covellite-sulfur-anglesite-atacamite-and other neomorphs paragenesis, of the absence of gold* in the ironstones (if we disregard the ironstones of the central part of the Northern Lens and the ironstones of the Intermediate Lens at 100 m. depths), and of the enrichment of these paragenetic minerals with arsenic. Our finds of visible gold at 15 to 20 m. distance from the contact with the ore inside a veinlet of gypsum, where cuprite and native copper were also present, are indications of a substantial migration of gold into the host rocks.

Molybdenum is present occasionally as traces in the Blyava primary ores. Oxidation and the secondary enrichment processes cause a progressive increase in the molybdenum content: up to 0.002% in the zone of the secondary enrichment; up to 0.006% in the leached zone and in the flint-gypsum loose material. Ironstones of the central part of the Northern and of the Intermediate Lenses contain hundredths of one per cent of Mo. The presence of molybdenum in mine waters and in neomorphs is a sign of its migration, although its migration ceases already at 68 to 76 m. below the surface and Mo is fixed in minerals of the veinlets. Figure 4 illustrates the enrichment of Mo. Molybdenum forms areas within the oxidized zone with its 10-fold enrichment, as against its concentrations in the ore body.

Thus the zones enriched by the Group II elements: arsenic, molybdenum, silver, lead, and barium (Figs. 3 and 4) embrace only the first few meters of the rock above its contact with the ore. The zones enriched by lead and especially by barium are somewhat broader in the deeper horizons. The mineral fixation forms are different in different zones for different elements: sparingly soluble sulfates (barite, anglesite), isomorphous replacements (e.g. of sulfur by arsenic), chlorides and sorption products (molybdenum, silver).

There are very regular relationships in the distribution of the Group elements in the course of the supergene alteration of ores and rocks (although the distribution is not always uniform), as well as in their distribution in the rocks subjected to the secondary alteration, surrounding the ore bodies, resulting in the development of enrichment zones at distances not exceeding 10 to 15 m. away from the contacts with the ore. This is both characteristic of the processes and highly important in prospecting and in reconnaissance.

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*The original is not clear as to whether it is gold or the entire paragenetic group that is absent in the ironstones. VPS

III. Lithophilic Elements

Ca, Mg, Na, Si, Fe,* Mn, V, etc. are the principal members of this group and they behave in a similar manner both in their ancient and in their modern migrations. During the oxidation processes within the ore body, the sulfuric acid waters exert a strong action on the contact areas transforming them into partly or entirely different rocks that preserve only relict structures of the original diabase or keratophyre. Such transformations always attracted the attention of prospecting geoogists and were used by them in recognizing the most promising areas in prospecting for ore bodies.

Since the Group III elements are most abundant in the host rocks as constituents of the rock-forming minerals, the scale of the transformations is great indeed, of transformations due both to ordinary weathering and to decomposition of the rocks by sulfuric acid waters. It is important, moreover, that, regardless of the scale of the alterations, the process is always in one and the same direction.

We observe a most drastic interaction between ore and host rocks—two very different materials—at 100 m. below the surface in the vicinity of Northern Lens of the Blyava. It is here, even now, that we observe a most intensive decomposition of the host rocks, the formation of new mineral species, the intensive migration of the ore constituents away from the ore body, and the accession of the lithophilic elements.

This view is sustained by the somewhat unusual behavior of some lithophilic elements, in this particular case, namely such as Mg, Al, Ti, as well as of some chalcophilic elements: Cu, Co, Zn, Ni, in their mutual association.

Two subgroups may be recognized among the lithophilic elements o Group III by the character of their migrations. One of them consists o Mn, Ca, Fe, Na, Si, V; the other one of Mg, Al, Ti. This second subgroup is conjoined with elements such as Zn, Cu, Co, Ni, as if it represented a lithophile-chalcophile transition, in its behavior in the migrations in the zones of oxidation and weathering.

Figures 5, 6, 7, and 8 represent the zones of enrichment with respect to different lithophilic elements. Figure 5 shows clearly that silicon forms an enrichment zone within the ore-rock contact band—a shirt of silica, as it were, enveloping the ores. The basic forms of silicon in this narrow zone at the contact are opal, chalcedony, and quartz. Farther away, this Si-enrichment zone grades into opal-jarosite in the hanging wall, and into silicified, bleached, and leached keratophyres and their tuffs in the footwall. Next, the Si-enrichment zone is overlain by the aluminum-enriched zone. Alterations in the

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*The iron bound in the host rocks.

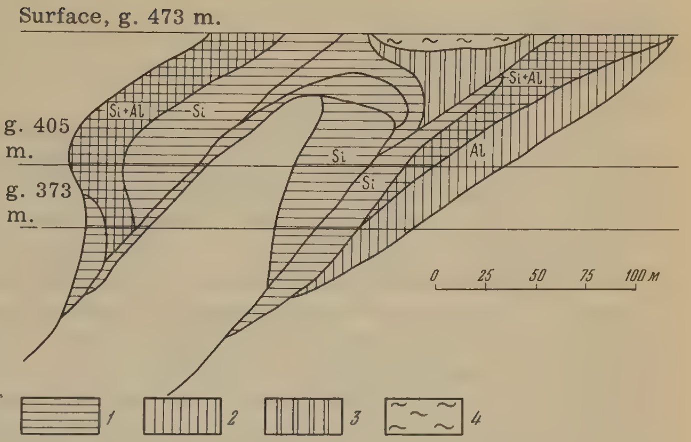

Fig. 5. Zones of enrichment by silicon and aluminum: 1-silicon enrichment zones; 2-aluminum enrichment zones; 3-iron oxide zone (gossan); 4-precipitated sediments.

mineral composition make it entirely clear that the opal-jarosites of the hanging wall are succeeded abruptly by bleached loose-grained diabases having abundant veinlets of mixtures of clay minerals: halloysite, metahalloysite, and kaolinite. Moreover, the bulk of the rock is halloysitized. The zone succession is just as clearly defined in the rocks of the footwall. Silicified varieties of acid rocks are succeeded by a zone abounding in veinlets of aluminum sulfates: first, aluminite and, next, alunite which is locally enriched with halloysite. The bulk of the rock (especially tuffs) is

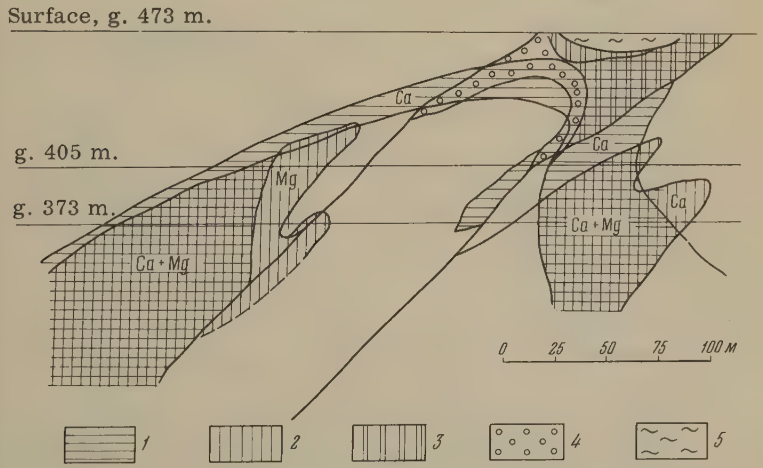

Fig. 6. Zones of enrichment by calcium and magnesium: 1-calcium enrichment zone; 2-magnesium enrichment zone; 3-iron oxide zone (gossan); 4-iron oxide-sulfate zone (jarosite); 5-precipitated sediments.

transformed into monothermites and hydromicas abundant in "nests" and spots of leuchtenbergite. This zone is succeeded, in turn, by the zone of less-bleached rocks which is literally saturated by alunite veinlets in its upper part and by aluminite veinlets at 76 m. depth, and deeper.

Figure 6 represents the calcium and the magnesium enrichment zones. It shows that magnesium, like zinc, is abundant only in the lowe horizons and that its principal form of fixation is the sulfate (epsomite) which penetrates and "soaks" the rocks of the lower horizons.

Calcium, on the contrary, has its enrichment zones in the upper part of the deposit where it forms a broad gypsum-rich band. Curiously, gypsum is found everywhere, beginning with the ore and ending with the host rocks at a considerable distance from the ore, whereupon it is succeeded by aragonite and, eventually, by calcite. Characteristically, to the measure of the distance from the ore body (and, consequently, to the measure of decreasing acidity), there is a gradation in the crystal forms of gypsum, from the selenite-type threads to "swallows' tails" and flat "pancakes". The same gradation is observed also in the carbonates, from aragonite (next to the ore) to calcite.

Figure 7 represents the manganese and the alkali (Na and K) enrichment zones. The manganese zone is especially well expressed in the diabases of the hanging wall, in the form of abundant black adhesions and veinlets within the decomposed loose-grained diabase. The manganese zone, from the surface down, is not traceable in the footwall rocks; a degree of enrichment with manganese may be seen only at 76 m. depth, and lower.

The manganese oxide zone in the footwall rocks is probably outside the range of our observation, as it is below the zone enriched by cuprite and by native copper.

The alkali-enrichment is expressed mineralogically by the appearance of jarosite and celadonite in the rocks of the hanging wall and of alunite (most commonly, sodian alunite) in the footwall rocks. This zone coincides with the zones enriched with silicon and aluminum.

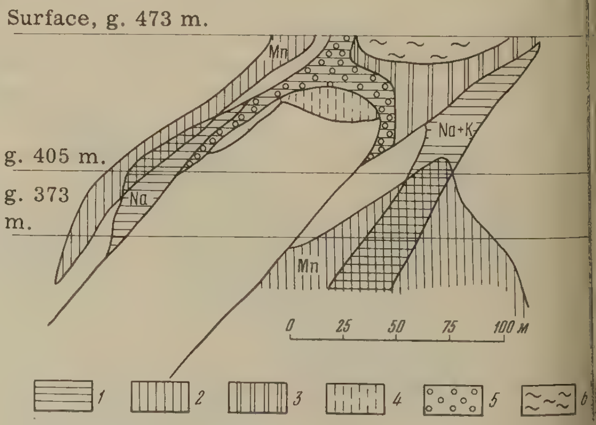

Fig. 7. Zones of enrichment by manganese, sodium, and potassium: 1-sodium and potassium enrichment zone; 2-manganese enrichment zone; 3-iron oxide zone (gossan); 4-flint-gypsum loose material; 5-iron oxide-sulfate zone (jarosite); 6-precipitated sediments.

Finally, Figure 8 represents the titanium enrichment boundaries in the host rocks. This enrichment is not appreciable (barely up to tenths, rarely up to a few per cent) and is observed not farther than 50 cm away from the ore. It depends chiefly on the leucoxenization of the disintegrated and leached rocks.

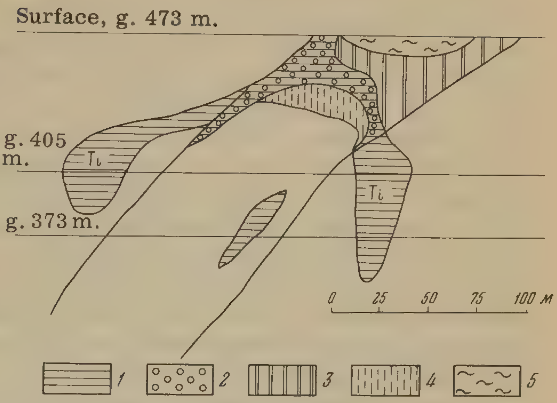

Fig. 8. Zones of enrichment by titanium: 1-titanium enrichment zone; 2-iron oxide-sulfate zone (jarosite); 3-iron oxide zone (gossan); 4-flint-gypsum loose material; 5-precipitated sediments.

Consequently, also in the instance of the lithophilic elements in the zone of the supergene alterations at the Blyava, there exists a definite geochemical zonation or rather a mineralogic-geochemical zonation, to the measure of the alteration of the host rocks. Silicification, jarositization, impregnation with gypsum, alunitization, and manganization are particularly well defined within the halo of the altered rocks. Knowledge of the successions in the development of the enrichment zones should help the prospector and the explorer in a reasonably rapid discovery of ore bodies.

V. *Other Elements*

All elements whose fixation forms are not known are referred by us to this group. The following two subgroups may be recognized, however:

1. Elements whose role is either obscure or insignificant. Chromium, zirconium, nickel, phosphorus, scandium, strontium, chlorine, bromine, and iodine belong to this subgroup. We have practically no data on their behavior in supergene processes. The mineral fixation forms are known so far only for phosphorus and for the halogens. These elements are probably of little interest in prospecting for pyritic deposits, since they do not yield either conspicuously characteristic minerals or any enrichment zones, since their distribution is sporadic and their quantities are small, serving merely to indicate a proximity of this or that kind of rock (chromium, nickel, scandium are associated generally with basic and ultrabasic rocks, etc.).

Indeed, phosphorus at the Blyava forms stable compounds with SO_4^{2-} ions (destinezite, etc.), in the specifically local environments, and becomes fixed in a direct proximity to the ore. We should always keep in mind the possibility of environments, analogous to the Blyava, occurring elsewhere.

2. The second subgroup, comprising Co, Sb, Sn, Bi, Cd, Se, Te, Ge, In, and also Be—the chalcophile companions of the ore bodies--present an especial interest in the geochemical prospecting for pyrite deposits. Beryllium is atypical for the Blyava, however, and is found there very rarely. Sb, Sn, Bi, Cd, Se, and Te are particularly important, on the other hand, because they are not parted from the ore body, in their migration, farther than 10 to 20 m. and they function accordingly as judicators of the ore body. The capacity of indium to become accumulated in the veinlets composed of highly dispersed clay minerals and of certain sulfates (alunites), in the upper horizons, in direct proximity to the ore, is important to remember in geochemical prospecting for deposits of pyrites. It is also important to know that these elements are detectable in dry residues of waters only at short distances from the ore bodies, not farther than 10 to 20 m.

Thus the role of the second subgroup of the Group IV elements consists characteristically of their relatively small migration capacity resulting in their local enrichment in certain areas and zones. This fact may be utilized in localizing pyritic ore bodies within their broad halos modified by the mineralizing metamorphism (including supergene metamorphism) of the host rocks.

PROSPECTING INDICATIONS

We are justified here, in view of the foregoing considerations, to make certain recommendations regarding prospecting for ores in the Blyava district, where there are about 30 economically promising areas at this time and where there is an abundance of rocks that were altered by the mineralizing supergene metamorphism. These promising areas ought to be surveyed geochemically, in order to ascertain the distribution of chemical elements and of minerals in the zones.

Even a cursory inspection of the erosion-shaped altered rocks near the ores may serve to find indications of an approximate position of an ore body. Clearly defined manganese-enrichment zones, at a greater distance from the mineralized zone, are favorable prospecting indications. This manganization is expressed as numerous and locally abundant veinlets or adhesions of the black manganese oxides in fissures. There may be even isolated lenses of manganese ore (like in the hanging wall of the Northern and of the Southern Lenses), in the instance of some far-advanced decomposition of the rocks. Where the alteration processes are not too far advanced, the manganization may appear in the form of small "nests", films, and veinlets. The manganese-enriched zones are especially well developed in diabases (the Northern Lens) and in flinty shales (the Northern and the West-Blyava Areas). The ore may be as far as 200 m., and farther, from such zones (for example, as at the Yaman-Kasy).

The copper-enriched zone is the next one and it is generally very much nearer than the manganized zone. The copper-enriched zone is

xpressed surficially in sporadic but fairly abundant copper carbonates:
zurite and malachite in the fissures, as films, adhesions, and veinlets.
uprite and native copper, in depths, are often in line with these surfi-
al expressions. The copper-enriched zones are discontinuous but
ey serve to outline the ore body boundaries, nevertheless, on all
des (both in basic and in acid rocks).

The copper- and manganese-enriched zones are observed most com-
only on slopes of hills or on the periphery of the water-divides (as at
e Blyavinskoe, Komsomolskii, and the Malachite Trench sites). This
ay be explained by their positions in the transitional zone, between
e unaltered and the disintegrated rocks. The disintegrated areas of
e diabase host rocks are also bleached and are enriched with alumina
d, to a lesser extent, with silica. The aluminum-enriched zone co-
cides most often, topographically, with shallow and local depressions
the ground. The adjoining zone is enriched by aluminum, silicon, and
e alkalies. Mineralogically, this zone is represented as follows: the
abases of the hanging wall are altered into halloysite or metahalloy-
te, and moreover, abound in the veinlets of these minerals. Closer
the ore, this zone is succeeded by the opal-jarosite zone. Jarositi-
tion is practically absent in acid rocks of the footwall where the rocks
e intensely alunitized instead. Next to the broad band of bleached
licified quartz keratophyres (from a few up to 50 m. thick), there lies
band of rocks that had lost the appearance of keratophyre or of its
ff and were transformed into a sticky monothermite-hydromica clay,
neycombed by veinlets of aluminite, in direct proximity to the ore;
vay from the ore, and toward the surface, aluminite is succeeded by
unite, in the veinlets. At the same time, alunite forms also ‘‘nests’’
d spots in the altered rocks and in the ironstones. Alunites in the
otwall rocks are highly enriched in indium, to the extent of 0.01 to
011%. Alongside indium, alunites of the Blyava contain about 0.00n%
, Ti, and Sc and up to 0.0n% Cu, Ca, and Pb.* Mining geologists
ght to consider especially the enrichment of the dispersed and of the
e elements in the alunites so abundant in the footwall rocks of the
rthern Lens. Alunites and alunitized rocks may be used as raw
aterials for the complementary recovery of the dispersed elements.

The more severely and the deeper were the host rocks decomposed
the sulfuric acid waters, the farther away from the ore are the
kali-enriched zones (alunite and jarosite). Locally, the alkali zones
ay be farther than 20 m. away from the ore body. We must re-
amine therefore the hypothetical Blyava ore field, for example, in
aces where jarosites were found without any underlying ores.

Thus, at the Blyava deposit there exists a horizontal sequence of the
nes enriched with lithophilic elements, to the measure of the dis-
nce from the rock-ore contacts: the zones of silicon, silicon and
minum, aluminum and the alkalies (in acid rocks), iron and the

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ectrographic analyses by 3 different laboratories.

alkalies (in basic rocks); there is an abundance of films, "nests", and lenses of manganese oxides at the boundaries of weakly altered or almost unaltered rocks. Magnesium is removed almost quantitatively, by leaching, from the upper to the lower rock horizons. Calcium is fixed as gypsum practically in all zones; the only differences are in th crystal forms of the calcium excretions. In weakly altered rocks, ten but not more than 100 meters away from the ore, calcium is fixed as aragonite; it is fixed as calcite at greater distances.

There is also a definite zonation in the supergene distribution of th principal chalcophilic elements (i.e., constituents of the bulk of the or body); iron (ore), sulfur, copper, and zinc, all of which are characteristically highly mobile in the oxidized zone. The halo of their dispersion is the broadest one and the forms of their fixation in minerals ar most highly varied but are controlled rigorously by the physico-chemical environments. The SO_4^{2-} ion combines successively with the following elements in the ore and along its contacts with the rock: a) lea (as anglesite) and other admixture elements which are indicators of o bodies; b) aluminum (as aluminite); c) aluminum and sodium (as alunite), or with iron (as jarosite or iron sulfates); d) finally, with calciu (as gypsum), and so forth. Iron is fixed successively, above the ore a at the contacts with the ore, as iron oxides, as jarosite, and—in depth—as secondary iron bisulfides and as complex sulfates, especially at the contact with the ore body. The bulk of zinc is leached out of the ore body, outwards and downwards, leaving only traces of its former presence, as in veinlets in the clayey neomorphs, in carbonates, and, more rarely, in ironstones.

As previously stated, copper is especially useful in prospecting, as it forms enrichment halos defining the boundaries of sulfide ore bodie and of disseminated sulfides which constitute also the ore field boundaries. The limited migration capacity of the chalcophilic admixtures group makes its member elements especially valuable in prospecting for pyritic ore bodies and in defining positions of such bodies in the altered zones of the host rocks. Detection of Pb, As, Se, Te, Mo, Ag, Sn, Sb, Bi, as well as of barium in anomalous quantities is an indicatio that the ore is not farther than 20 to 50 m. away.

Among the rare and the dispersed elements, indium and cadmium may be used as indicators. Indium often forms accumulations (tenths and hundredths of one per cent) in alunitized rocks and in alunites at distances up to 50 m. from the ore.

There is a vertical mineralogic sequence of the zones of the enrichment with different elements. The mineralogic composition varies progressively in every zone, from top to bottom. For example, the iron-enriched zone shows the following succession of its minerals: at the top—iron oxides; next—iron sulfates; finally—secondary bisulfides of iron. For the copper-enriched zone: malachite at the top, together with azurite and tenorite; next—cuprite and native copper; finally—secondary copper sulfides, first—covellite, and next—chalcocite. In such manner, examination of the areas in depth, in mine workings and boreholes, provides supplementary data that make the surficial studies more exact. We must keep in mind also that supergene alterations of rocks cease at certain depths and that the halo of altered rocks is funnel-shaped.

The extensively developed ferrugination in fissures and in the rock itself camouflages the exact zone boundaries and makes it difficult, on the first visual inspection, to "decode" the indications in the field.

Iron forms a series of enrichment zones (Fig. 1) of which the main one is the gossan itself which overlies the ore body outcropping at the surface. If the ore body is blind, the ferruginized zones may be found at an appreciable distance from the ore. In a case of this sort, spectrographic analysis of the ferruginized rocks must come to our aid.

The following chalcophilic admixture elements are detectable spectrographically in rocks directly next to the ore body: silver, gold, lead, arsenic, molybdenum, and also barium, indium, tin, bismuth, cadmium, antimony, selenium, tellurium, germanium. It is not at all essential to prove the presence of all of these elements, but only of some of them, because their enrichment zones are discontinuous and because their amounts in the ore are small.

Breadth of individual zones and their distances from the ore depend chiefly on the intensity and the duration of supergene processes to which the host rocks of the ore body were subjected. The halos of disseminated sulfides surrounding the ore bodies exert a major influence here, as they increase the breadth of the bands of altered rocks and cause displacements of some of the zones. As shown by the example of the Northern Lens, the most extensive alteration takes place in the footwall rocks, while, in the rocks of the hanging wall, on the contrary, the entire sequence of the zonations may be observed in one single pit, in an open cut (20 to 30 to 50 m. across), although the delineation of these zones is probably at its clearest in the hanging wall, if we disregard the overlapping of the zones enriched with silicon, sodium, and iron in the opal-jarosite rocks.

The mineralogic-geochemical method of study of areas under prospecting should be applied concurrently with mine workings of the light type, with drilling, and especially with geologic surveys.

CONCLUSIONS

A series of relationships in the behavior of chemical elements and in their distribution in the ore body and in the host rocks was indicated by our studies of migration of the elements within the oxidized zone of he Blyava deposit. These relationships may be summarized as follows:

1. Three distinctive groups of elements are recognized, in reference to similarities in their behavior in the migration during the supergene processes.

2. Our studies show that there is a definite direction in the migration processes resulting in a dispersion of the ore constituents in the host rocks and also in a sorting of individual elements at certain distances from the ore bodies, depending chiefly on the depths of penetration of the supergene processes as well as on the environment wherein these processes are operative. External changes in the environmental factors (climatic, tectonic, hydrodynamic regime of waters, marine transgressions, burial under marine sediments, thickness of the ore bodies, their surficial exposures, character of the host rocks, etc.) have major effects on the intensity and the rate of the supergene processes, without affecting their general direction.

3. There exists a supergene mineralogic-geochemical zonation for a series of chemical elements around ore bodies and ore fields, both vertical and lateral. The discrete enrichment zones may locally coincide or overlap each other, while elsewhere they may differentiate clearly, depending on the duration of the supergene effects and on the intensity of the migration processes.

4. The succession of supergene altered zones in the prospected areas which were investigated geochemically and mineralogically may give a fairly exact idea to the prospecting geologist as to the position and the depth of an ore body and of its probable composition. One must pay attention, in such conditions, to the fixation forms of individual elements in different minerals and mineral species (for example, in the case of gypsum, as one goes away from the ore body, laterally, the needle-like and columnar crystal forms in the ore are succeeded by veinlets of the selenite type which are followed, in turn, by impregnations of the rocks with uniformly oriented flat crystals; the latter are succeeded by crystals of the ''swallow-tail'' type and by small flat lenses, which, in turn are succeeded by calcium carbonates, first by aragonite and then by calcite). Minerals and mineral species are also distributed regularly, in a definite sequence, around the ore bodies.

5. The relationships here shown, in the instance of the supergene altered rocks of the greenstone belt in the Blyava district, in the vicinity of the pyritic deposits, may be used in prospecting and exploration in analogous geologic environments in other districts.

REFERENCES

1. Brodskii, A. A. Gidrokhimicheskii Metod Poiskov Medi (The hydrochemical method of prospecting for copper). *Geolizdat.* 1956.
2. Vinogradov, A. P., M. S. Chupakhim, V. A. Grinenko, and A. V. Trofimov. *Geokhimiya* No. 4, 1956.
3. Herman, L. D. O Destinezite v Zone Okisleniya Kolchedannogo Mestorozhdeniya Blyava na Yuzhnom Urale (Re destinezite in the oxidized zone of Blyava, a pyrite deposit, Southern Urals). *Zap. Vsesoy. Mineralog. O-va, Akad. Nauk SSSR,* Moscow-Leningrad, Ser. 2, ch. 85, 1956.

4. Zavaritskii, A. N. Metamorfizm i Metasomatizm v Ural'skikh Kolchedannykh Mestorozhdeniyakh (Metamorphism and metasomatism in pyritic deposits of Ural). *Sb. Kolchedannye Mestorozhdeniya Urala, Akad. Nauk SSSR, IGN* (Inst. Geol. Sciences), 1950.

5. Karyukina, V. N. Opredelenie pH Suspenzii Mineralov (Determination of the pH of mineral suspensions). *Gosgeoltekhizdat,* 1953.

6. Kreiter, V. M. Materialy K Voprosu o Migratsii Zolota (Materials in reference to the migration of gold). *Tr. MGRI,* t. 17, 1941.

7. Nekrasov, B. V. Obshchaya Khimiya (General chemistry). *Goskhimizdat,* 1954.

8. Razumovskii, N. K., E. V. Voinova, E. E. Razumovskaya, and A. V. Khabakov. Geologicheskoe Stroenie Blyavinskogo Kolchedannogo Mestorozhdeniya na Yuzhnom Urale (Geologic structure of the Blyaya pyrite deposit, Southern Ural). Rukopis (ms.), 1934. *Fondy Blyav. GRP* (The Blyavas File, GRP).

9. Rogover, G. B. Mednokolchedannoe Mestorozhdenie Blyava (The chalcopyrite deposit of Blyava). *GONTI.* 1939.

0. Shadlun, T. N. *Tr. IGN Akad. Nauk SSSR,* Ser. Rudnykh Mestorozhdenii (Trans. Inst. Geol. Sciences, Ore Deposits Ser.), Vyp. 96, No. 11, 1948.

1. Khitarov, N. I., and E. P. Mulikovskaya. K Geokhimii Rudnichnykh Vod Sul'fidnykh Mestorozhdenii (Geochemistry of mine waters of sulfide deposits). *Problemy Sovrem. Geol.* No. 8, 1935.

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THE ROLE OF IRON SULFIDES IN THE ACCUMULATION OF MOLYBDENUM IN SEDIMENTARY ROCKS OF THE REDUCED ZONE

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Abstract

The role of iron sulfides in the process of molybdenum accumulation in sed mentary rocks enriched in organic matter is being determined. It is shown experimentally that molybdenum amounting to 70-96% of the total content, accord to conditions, is co-precipitated with iron sulfides from solutions whose compositions are approximately similar to natural solutions. The study of natural iron sulfides has shown that most of the molybdenum is concentrated in melnik vite, apparently in the form of a sorbed sulfide compound. Coarsely-crystallin pyrites contain minor amounts of molybdenum, due to loss of molybdenum in th aging process. Thus the bond of molybdenum in sedimentary rocks with horizo enriched in sulfides is of a regular character. This regularity is to a certain degree true also for elements associated with molybdenum—Ni, Co, V, etc.

A large body of data on distribution of molybdenum in sediments of the reduced zone (carbonaceous and bituminous rocks) has been accum lated in the past decade, chiefly in connection with studies of possibili ties of comprehensive utilization of mineral raw materials [15, 17, 18 21, 25, 26] etc. This large body of data enables us to supplement and to refine the existing concepts of the relationships involved in the accu mulation of molybdenum in the materials in question. The most popul view, in this respect, was formulated by V. M. Goldschmidt [18], to th effect that the bulk of molybdenum is accumulated as jordisite (MoS_2), a finely dispersed sulfide, with the participation of hydrogen sulfide; this mineral is found in the cupriferous Permian shales of Germany. This view implies that organic substance has only indirect influence o the accumulation of molybdenum, acting merely as a source of hydrog sulfide under certain conditions. P. K. Kuroda and E. B. Sandell [21] adhere to this same interpretation in their recently published summar of geochemistry of molybdenum, and so do a number of other investigators [6, 8, 26], etc.

The bulk of molybdenum is associated with the light-weight fractio consisting almost entirely of organic substance, as is shown by the fractional analysis. This fact has led several investigators [9, 25] to the assumption that molybdenum is fixed chiefly in the organic substa that is responsible for the accumulations of molybdenum. K. B. Kraus kopf [20] also presumes, while studying precipitation of certain rare elements from sea water, that organic substance is paramount as the accumulator of molybdenum and that the mechanism of the accumulation is adsorption.

There arises the following problem: What is the real mechanism of the accumulation of molybdenum--is it the precipitation of molybdenum as the sulfide or is it its adsorption by organic substance? Or perhaps are both processes operative in nature but in different environments? We shall be able presently to show that the available data lead us to the belief that there exists only one of these processes which is responsible for accumulation of molybdenum.

Relationships involved in the accumulation of molybdenum are naturally more conspicuous in the rocks containing anomalous quantities of this metal. It is of interest, in this connection, that molybdenum "highs" in the rocks of the reduced zone are found in horizons more or less enriched by sulfides [6, 21]. Reports of molybdenum "highs" (up to 0.1%) in the pyritic fraction of the rocks here discussed [9, 15] have a direct bearing on the problem in question.

The close association of molybdenum with sulfides in nature, together with its chemical properties, namely, its inability to be precipitated directly by the sulfide in marine environments (pH 7 to 8), on account of the formation of easily soluble thio compounds of molybdenum, give us sufficient reasons for supposing that the co-precipitation of MoS_2 and FeS_2 is by no means a minor factor in accumulations of molybdenum. In order to test this supposition we investigated experimentally the co-precipitation of molybdenum and iron sulfides.

EXPERIMENTAL PROOF OF POSSIBILITY OF CO-PRECIPITATION OF MOLYBDENUM AND IRON SULFIDES

Data on this possibility are very scarce in the literature. It has been established empirically that the co-precipitation may indeed take place, provided the solubility product of the co-precipitating component is smaller than the solubility product of the collector [13]. The co-precipitation of molybdenum with iron sulfides is entirely possible from such point of view. However, K. B. Krauskopf [20] pointed out that the co-precipitation of molybdenum and its close associates (Ni, Co, V) with FeS_2 is a minor factor in the accumulation of molybdenum by rocks rich in organic substance. It is not quite clear just what Krauskopf did have in mind, but experiments by other investigators, together with certain facts, show the opposite of his conclusion. Thus it has been demonstrated that nickel may be accumulated from dilute solutions by co-precipitation with FeS_2 [13]. The same possibility exists also for molybdenum, as may be inferred from the experiments performed by the author. As to cobalt and vanadium, examples of their "highs" in pyrites from naturally formed materials [1, 8] are indicative of the probability of their accumulation in sediments by means of co-precipitation with FeS_2.

The co-precipitation phenomena were studied by different investigators from the analytical-chemical point of view [5, 10, 11, 13, 19], etc The problem is still obscure in the geochemical literature and it is necessary, for that reason, to consider here certain fundamental propositions in brief. The co-precipitation is regarded as a "drag", a capture of various admixture elements by a precipitate in the course o its formation, with the understanding that the elements so captured do not form independent precipitates, in the given environment, but form colloidal or true solutions instead. The capture of the admixtures ma be contingent upon different mechanisms among which, in nature, sorption and ionic exchange are apparently the most common ones. The co-precipitated trace elements may be held by the adsorption forces or may form solid solutions or chemical compounds with the sediments.

In our experiments, the sediment in question was FeS_2 and the captured admixture was molybdenum which cannot be precipitated independently by hydrogen sulfide from solutions at the pH levels (4 to 9) that are characteristic of natural processes. The trace elements (Co, Ni, V, Cu, Mo, Tl, etc.) in nature may be termed the co-precipitated admixtures that are present in iron and manganese ores, pyrites, galenas, and other minerals. The co-precipitation is influenced by relative proportions of the admixtures and the collectors, by their absolute concentrations, by temperature, time, presence of other ions and pH of the solution. Co-precipitation is highly significant in the distribution of the rare elements at high temperatures and pressures [16].

METHODS

The precipitation was carried out from 1-liter volumes of solutions containing different amounts of molybdenum and iron: the molybdenum standard from ammonium molydate, $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$; the iron was ferrous sulfate, $FeSO_4$. An aliquot of ferrous sulfate solution was placed in a 1-liter volumetric flask to which measured volumes of the molybdenum standard were added, as well as sodium hydroxide or sulfuric acid (for the desired pH), and other reagents whose effects on th co-precipitation were to be investigated. Concentrations of the hydrogen ions were determined by the lamp potentiometer of the LP type. I the resulting solution, at pH > 5, there was a formation of greenish flakes of iron hydroxide which were partially oxidized by the air, judging by their brown tinge. It was shown experimentally, however, that the extent of the oxidation of iron has no influence on the results of the co-precipitation. Hydrogen sulfide was passed slowly through the suspension, after a thorough shaking of the solution, to the point of saturation [10]. After attainment of equilibrium, in 2 to 3 days, the suspension was passed through sintered glass filter No. 4, feeding it to the filter through glass tubes connected to the flask, in order to minimize oxidation of the sulfides by the air. Molybdenum was determined in th

trate colorimetrically. Differences between replicate determina-
ns did not exceed 5%. All experiments were conducted at room
mperature (18 to 22°C), fluctuations of which had no observable ef-
ts on the results of the determinations.

It is known that a lowering of the pH takes place during precipita-
n of sulfides under conditions of our experiments. However, if the
ution contains soda neutralized by sulfuric acid to pH 7-8, there is
lowering of the pH. The mixture of Na_2SO_4 and $NaHCO_3$ produced
the neutralization functions evidently as a kind of a buffer.

periment I. Possibility of Independent Precipitation of Molybdenum Hydrogen Sulfide

As is known in analytical chemistry, a quantitative precipitation of
lybdenum as MoS_3 is possible in strongly acid media and is associ-
d with appreciable difficulties. This is due to the tendency of
lybdenum toward reduction by hydrogen sulfide and to its partial
nsition into the colloidal state [24]. We were not able to find in the
rature a procedure for a possible precipitation of molybdenum by
rogen sulfide in weakly acid media, i.e., from solutions resembling
natural ones (pH 3 to 6). It was made clear experimentally that, at
molybdenum content of the solution ranging from 1 x 10^{-3} to 1 x
^{4}%, in the presence of 30 grams/liter of NaCl, with the terminal pH
to 6, after passing H_2S through the solution for 20 minutes, the re-
is a transparent amber-yellow colloidal solution of MoS_3. This
ution loses some of its transparency after 2 to 4 days storage in the
ence of air, without yielding any sediment, although it may be co-
lated by large amounts of an electrolyte (100 to 150 g/l NaCl).
bility of the colloidal MoS_3 solution increases markedly at a more
line pH. Thus at pH6, there was no sediment obtained from the
S_3 colloidal solution after one month and a half, whereas the same
ution at pH3 produced a sediment, a gel, on the fourth or the fifth
of storage.

t is known that easily soluble thiomolybdates are formed in alkaline
lia after passage of hydrogen sulfide through solutions containing
$_4^{2-}$ ions [24]. They are formed by a gradual replacement of the
gen by the S^{2-} ion: $Na_2MoO_3S \rightarrow Na_2MoO_2S_2 \rightarrow Na_2MoS_4$. We showed
erimentally that the formation of thiomolybdates is characteristic
for solutions resembling natural solutions in their properties at
7.2 and still more alkaline. Salinity of the test solutions in which
thiomolybdates were observed was as follows: 20 g/l NaCl; 6 to 8
Na_2SO_4; 3 to 5 g/l $NaHCO_3$. As stated under "Methods", this
ture inhibits the lowering of the pH after a passage of hydrogen
de. In such manner, at pH about 6 and in the presence of H_2S,
bdenum forms stable colloidal solutions but forms easily soluble
nolybdates at pH 7.2 and higher. Consequently, molybdenum can-
pass into the sediment independently.

Experiment II. Co-Precipitation of MoS_3 and FeS_2 in Solutions Without Electrolytes

The quantities of iron in our series of experiments were 0.2 and 0.02 g/l (i.e., 1.0 and 0.1 g $FeSO_4 \cdot 7H_2O$) or 2×10^{-2} and 2×10^{-3}%. The quantities of molybdenum varied from 10^{-5} to 10^{-2} g/l or from 1×10^{-6} to 1×10^{-3}% correspondingly. The greenish flakes of ferrou hydroxide forming on the alkaline side of pH5, under the experimenta conditions, together with the ferric hydroxide derived from the ferrou by oxidation, adsorb 82 to 90% of the molybdenum. However, there is a desorption of molybdenum, on the passage of H_2S, followed by a formation of a colloidal solution of molybdenum trisulfide at pH < 7 or b formation of thiomolybdates at pH on the alkaline side of 7. This cou be proved in the following manner: If, one hour after the passage of H_2S and of the formation of the black iron sulfides, the filtrate of the suspension is examined, its color will be characteristically the color of the colloidal MoS_3 or of the thiomolybdates, while if the filtrate is examined after attainment of the equilibrium, it will prove to be colorless. Colorimetric analyses of the colored filtrate show the presence of 70 to 76% of the molybdenum in the original solution. Thus we are dealing with a sequence of precipitations, in our experiments, brough about apparently by interactions between two sols of MoS_3 and FeS_2. Although the kinetics of this process was not studied in detail, we wer able to show nevertheless that it takes about 20 hours for the equilibrium to be established.

The co-precipitation of 10 to 1000 micrograms/liter of molybdenu (10^{-6} and 10^{-5}% respectively) with either 0.2 or 0.02 g/l of iron is practically quantitative, at the terminal pH6, since no molybdenum is detectable in the filtrate within the sensitivity limits of the colorimetric method. Under the same conditions, with 0.2 g/l iron and $1 \times 10^{-}$ molybdenum, the percentage of the Mo co-precipitation is 98.5, but it is only 91.3 if the iron is one-tenth of the former amount, i.e., 0.02 g

The most convenient amounts of iron and molybdenum, 0.2 and 1 x 10^{-2} g/l respectively, were employed in ascertaining the relationship between the pH and the completeness of the co-precipitation. The results are presented in Table 1; the pH of the solutions, here and later in the report, refer to solutions after the passage of H_2S.

According to Table 1, the per cent co-precipitation ranges from 97.2 to 81.5 within the pH limits of 5.3 to 8.7. The minimum of the c precipitation, 81.5%, is observed in the alkaline medium. This may b explained best by the formation of soluble thiomolybdates in such environments instead of the colloidal solutions that are formed in weakl acid media at pH < 7.0.

Table 1

Present in solution, g/l		pH of solution	Amount of co-precipitated Mo	
Mo	Fe		grams	%
1×10^{-2}	0.2	5.3	0.00972	97.2
1×10^{-2}	0.2	6.8	0.00904	90.4
1×10^{-2}	0.2	8.7	0.00815	81.5

xperiment III. Effect of Electrolytes on Co-Precipitation

We know that solubility of different compounds depends also on salts resent in the solution. It became necessary therefore to ascertain is effect on the co-precipitation of the constituents here discussed. he salts were chosen on the basis of the V. V. Krasintseva's studies f the ground waters from Tertiary sediments [7], on the assumption at such composition is characteristic of the diagenetic stage, on the rst approximation. The experimental conditions and the results are ated in Tables 2 and 3.

On consideration of Tables 2 and 3, one may see that the amounts of e co-precipitated molybdenum increase parallel with the amounts of on. If, at pH 6.4, there is 1×10^{-3}% Mo in the solution, in the pres- nce of 0.02 g/l Fe (Table 2) the per cent of co-precipitation is 69, but is 98 at 1 g/l Fe, all other things being the same.

The same relationship is also observed at different pH levels and at alitatively different salinities of the system. Thus the data in Table show that at pH 7.8, as the concentration of Fe increases from 0.02 to 0 g/l, with Mo being constant at 1×10^{-3} g/l, the per cent co-precipi- tion increases from 70 to 93. Moreover, there is also a certain de- ease in the amount of the co-precipitated constituent at increasing I, which is most likely due to the formation of colloidal solutions of oS_3 in weakly acid media and of thiomolybdates in alkaline media, as ready stated. The amounts of co-precipitated molybdenum increase

Table 2

esent in solution, g/l		pH of solution	Electrolytes, g/l	Amount of co-precipitated Mo	
Mo	Fe			grams	%
10^{-3}	0.02	6.4	-	6.9×10^{-4}	69
10^{-3}	0.20	6.3	30 ; NaCl	7.8×10^{-4}	78
10^{-3}	1.00	6.3	-	9.8×10^{-4}	98
10^{-2}	0.20	6.5	-	7.5×10^{-3}	75

Table 3

Present in solution, g/l		pH of solution	Electrolytes, g/l	Amount of co-precipitated M	
Mo	Fe			grams	%
1×10^{-3}	0.02	6.9	20 ; NaCl	8.2×10^{-4}	82
1×10^{-3}	0.02	7.8	-	7.0×10^{-4}	70
1×10^{-3}	0.20	6.9	6; 8; Na_2So_4	8.9×10^{-4}	89
1×10^{-3}	0.20	7.8	-	7.6×10^{-4}	76
1×10^{-3}	1.0	7.8	3; 5; $NaHCO_3$	9.3×10^{-4}	93
1×10^{-4}	0.2	7.2	-	9.9×10^{-5}	99

in the presence of $NaHCO_3$, which may be due to the capacity of soda to absorb H_2S, which, in turn, results in increased concentrations of the S^{2-} ions in the solution. This capacity of aqueous solutions of sod is utilized in industry in the liberation of the coking gases from hydrogen sulfide [4]. Consequently it is not the pH of the solution, but the presence of sodium bicarbonate by which the marked increase in the concentration of the sulfide ions is brought about, that exerts the mos important influence on the co-precipitation. This is especially to be remembered, because an analogous phenomenon may be operative als in natural processes, as has been pointed out by several investigators in regard to the formation of alkali carbonates, as intermediate diagenetic products from CO_2 produced by organic substance [7].

Our experiments serve to demonstrate, in such manner, that the molybdenum "highs" in sulfide-rich horizons of sedimentary rocks are not accidental but are explainable rationally by the co-precipitatio of molybdenum with FeS_2.

The quantities of the co-precipitated constituents may either decrease or increase during aging of the sediment (FeS_2). Although the were no separate experimental studies of the behavior of molybdenum during aging of iron sulfide, its behavior may be ascertained indirectl by observations in nature. With this purpose in mind, we isolated a finely dispersed iron sulfide (melnikovite) from a sooty horizon* of Tertiary sediments, by centrifuging the sediments in bromoform (sp. gr. 2.8), not without an admixture, of course, of some other finely dispersed minerals. Chemical analysis showed 41.1% iron sulfide and 18.6% of the admixtures of other minerals. The proportion of the admixtures, most of which were terrigenic, here shown is markedly too low because they could be isolated in their relatively pure state only after treatment with aqua regia for 40 minutes on a steam bath. Naturally, the bulk of the minerals was dissolved under such conditions.

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* "Sazhistyi gorizont"; a horizon containing black pulverulent substance, like severely weathered dust-like coal, by which hands may be stained. In this ca the black dusty sulfides are probably meant. VPS

xamination of thin sections of the melnikovite powder suggested that e mineral fraction amounted to at least 40 to 45%. Curiously it was so noted that the iron sulfides form envelopes around the other min-rals, i.e., that the iron sulfides are formed at the surface of the other inerals. There was 0.072% molybdenum in the melnikovite isolated us, but only 8.5 x 10^{-4}% molybdenum in the coarsely crystalline rite (0.1 to 3 mm), whereas molybdenum was only 4 x 10^{-4}% (aver-e of 3 determinations) in the pyritic concretions from the same oty horizon. Considering the distribution of molybdenum between elnikovite and pyrite, in this case, one may be inclined to conclude at molybdenum is withdrawn from melnikovite by the aging process. t is it true that melnikovite is indeed different from pyrite by the gree of its aging? In order to answer this question, let us examine w some data on melnikovite from the available literature together th some first-hand observations by the author.

It is known that, in the aging process, there is a contraction of the ystal structure of the precipitate which is generally accompanied by recrystallization. Depending on the duration of the process, the more arsely crystalline particles are the result of the recrystallization. sofar as the aging process is characterized by structural changes, it reasonable to compare melnikovite and pyrite by the means of their -ray diffraction patterns.

A. G. Betekhtin [2] believes that natural melnikovite is not an inde-ndent mineral because its X-ray diffractions are sometimes like the ffractions of pyrite and sometimes like marcasite. However, the ta presently to be reported dealing with synthetic and natural iron lfides make it doubtful whether the finely dispersed melnikovites, olated with care by the centrifuge method, could yield the diffraction tterns of either pyrite or marcasite. Thus Lepp [22], in his studies aging of a synthetic FeS_2, reports a diffraction pattern that has thing in common whatsoever with the standard patterns of pyrite or arcasite (Table 4).

G. Rosenthal [28], in his studies of synthetic iron sulfides, had also tained X-ray diffraction patterns that were different from the stand-ds. True, he regarded his patterns as anomalous, on account of a rmation of a hypothetical alkali-iron complex of the $Na_5(Fe(OH)S_3) \cdot$ O type. This explanation is not very convincing, however. Even if ere were such complexes at all, the amount of sodium in solution at 8 to 10 would be far from sufficient for its fixation in an iron sul-le complex, under the experimental conditions (FeS_2 was produced om 5 grams of $FeSO_4 \cdot 7H_2O$, while the sodium content of the solution uld not be over 0.2 to 0.5 grams).

In his studies of the products of the co-precipitation, the author had so obtained an X-ray diffraction pattern which was different from the ndard pyrite and marcasite patterns (Table 4). This pattern, re-rted in Table 4, shows no resemblance whatsoever to the pattern ained by Lepp (Table 4). Such roentgenometric differences between

Table 4

Synthetic melnikovite				Natural melnikovite (Author's data)		Standard			
According to Lepp		According to author				Pyrite		Marcasit	
d	I	d	I	d	I	d	I	d	I
3.80	2	3.20	1	4.81	8	3.102	2	3.428	
3.45	2	3.10	2	3.62	9	2.696	8	2.690	1
3.27β	2	2.81	10	2.64	10	2.417	8	2.412	
2.96	9	2.45	0.5	1.96	6	2.206	7	2.314	
2.71	1	2.20	3	2.80	4	1.908	6	2.051	
2.46	9	1.99	10	1.70	6	1.629	10	1.908	
2.09	1	1.78	1	1.63	5	1.560	3	1.868	
2.01	1	1.69	1	1.55	4	1.498	4	1.754	1
1.92β	3	1.62	8	1.50	3	1.444	6	1.720	
1.89	4	1.40	6	1.37	2	1.239	3	1.689	
1.83	1	1.39	2	1.30	5	1.208	4	1.673	
1.739	10	1.26	9	1.27	4	1.179	4	1.593	
1.561	1	1.15	8	1.23	3	1.103	5	1.499	3
1.507	1	-	-	1.21	7	1.040	6	1.428	5
1.420	-	-	-	1.12	5	-	-	1.365	4
1.283	1	-	-	1.076	5	-	-	1.209	2
1.231	1	-	-	1.057	5	-	-	1.204	2
1.140	1	-	-	1.036	4	-	-	9.190	3
1.102	2	-	-	1.018	4	-	-	1.164	4
1.007	6	-	-	1.011	3	-	-	-	-

Conditions of record by the author: Fe anticathode; manganese filter; D = 57.3; 35 kv; 10 m.a.; alpha-radiation.

Photography and calculations by A. K. Fedotova, Laboratory of Crystal-Chemistry Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR.

the synthetic iron sulfides may be due, in all probability, to the fact that only a few days were allowed for aging of the precipitate, in Lepp' experiments, while in ours the aging was prolonged considerably, namely, for 35 days. The sulfides of iron were produced from weakly alkaline media in both experiments; both yielded the patterns of pyrite upon heating in a sealed ampule. The pattern of melnikovite (Table 4) isolated by us from Tertiary sediments was also different from the standard pyrite and marcasite patterns and also from the pattern of smythite, a recently discovered iron sulfide [27]. The melnikovite here examined contained admixtures of other minerals, but mechanical admixtures of this sort may only complicate the pattern without affecting presence of either pyritic or marcasitic lines in the pattern.

The foregoing facts enable us to suppose that, from the moment of the formation of hydro-troilite ($FeS \cdot nH_2O$) to the time of its complete conversion into a coarsely crystalline pyrite, there exists a series of intermediate stages of the minerals, of which melnikovite is one, grading one into another in the course of the aging. Consequently, we must agree with Lepp [22], in his recognition of melnikovite as an dependent mineral differing from pyrite in its crystal structures. e must remember nevertheless that melnikovite is one of the most able products of the aging of iron sulfide, in the transformation ries, from hydro-troilite to pyrite or marcasite. In this connection, e presence of molybdenum "highs" in melnikovite and the very low olybdenum content of pyrite become fully understandable, if we conder that molybdenum is abstracted from pyrite, during the aging, ., during the transition from melnikovite to pyrite.

CONCLUSIONS

1. It was shown experimentally that molybdenum is co-precipitated th iron sulfide from solutions resembling natural ones in their saity. 70 to 96% Mo may be so co-precipitated, depending on condins of the experiments. This co-precipitation is an important factor cordingly in the accumulation of molybdenum in sedimentary rocks, d the association of molybdenum with sulfide-rich horizons of sedients is entirely normal.

2. Molybdenum is accumulated in finely dispersed sulfides of iron elnikovite) by a sorption of its sulfide. The almost complete absence molybdenum in coarsely crystalline pyrites may be explained by rese of molybdenum during their aging.

3. Deductions regarding the preponderance of the association of olybdenum with organic substance in coals and in organic shales are malistic. Their error is due to the under-estimation of the presce and the effects of the finely dispersed pyrite in the organic subnce even in a centrifuge. And yet it is in this very kind of pyrite t the molybdenum "highs" are found, as, for example, in the innce of carbonaceous-siliceous shales.

4. The regular association of molybdenum with iron sulfides in dimentary rocks extends also to include its associates, Ni, Co, and and may be used as a prospecting indication for rare elements in diments, especially since we know very little about rare elements such, in sedimentary rocks [3].

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REFERENCES

Beneslavskii, S. I. Perspektivy Kompleksnogo Ispol'zovaniya Boksitov (The perspectives of the comprehensive utilization of bauxites). *Tsvetnye Metally*, No. 1, 1957.

Betekhtin, A. G. Mineralogiya. *Gosgeolizdat*, 1950.

3. Ginzburg, I. I. Opyt Razrabotki Teoreticheskikh Osnov Geokhimicheskikh Metodov Poiskov (An essay in theoretical development of the premises of geochemical prospecting). *Gosgeolizdat,* 1957.
4. Egorov, N. N., M. M. Dmitriev, and D. D. Zykov. Ochistka ot Sery Koksoval'nykh i Drugikh Goryuchikh Gazov (Purification of coking and other gases from sulfur). *Metallurgizdat,* 1950.
5. Kolthoff, I. M., and E. B. Sandell. Kolichestvennyi Analiz (Quantitative Analysis). Izd. IL, 1948.
6. Korolev, D. F. Nekotorye Osobennosti Raspredeleniya Molibdena v Porodak Bylymskogo Ugol'nogo Mestorozhdeniya, Severnyi Kavkaz (Certain features of the distribution of molybdenum in rocks of the Bylym coal deposit, Northern Caucasus). *Geokhimiya,* No. 5, 1957.
7. Krasintseva, V. V. Sostav Rastvorov iz Porod Esentukskogo Mestorozhdeniy Mineral'nykh Vod (Composition of solutions from rocks of the Essentuki deposit of mineral waters). *Sov. Geolog. Sb.*, 56, 1956.
8. Lebedev, L. M. Sul'fidy Polimetallov i Nikelya v Yurskikh Otlozheniyakh Podmoskov'ya (Sulfides of polymetals and nickel in Jurassic sediment of Moscos district). *Doklady Akad. Nauk,* New Ser., No. 2, 1954.
9. Razumnaya, E. G. Izuchenie Raspredeleniya Molibdena i Vanadiya v Uglist Kremnistykh Slantsakh Metodon Tsentrifugirovaniya (Studies in the distribution of molybdenum and vanadium in carbonaceous-flinty shales by the centrifuge method). *Sovrem. Metod. Mineralog. Issled. Gorn. Porod, Rud. i Mineralov, Sb. st. VIMS'a. Gosgeoltekhizdat,* 19
10. Rudnev, N. A., and L. I. Guseva. O Sorbtsii Nekotorykh Poverkhnostnoaktiv Krasitelei Sul'fidami v Protsessakh Ikh Stareniya (In reference to the sorption of some activated dyestuffs by sulfide in the process of their aging). *Zh. Analit. Khim.*, XI, Vyp. 1, 1956.
11. Rudnev, N. A., and A. A. Mazur. Issledovanie Mekhanizma Soosazhdeniya Kationov s Sul'fidami pri Pomoshchi Radioaktivnykh Izotopov (Investigations of the mechanism of the co-precipitation of cations an sulfides with the aid of radioactive isotopes). *Zh. Analit. Khim.*, XII, Vyp. 4, 1957.
12. Strakhov, N. M. Osadki Krupnykh Vnutrikontinental'nykh Vodoyomov SSSR. Obrazovanie Osadkov v Sovremenykh Vodoyomakh (Sediments of the large continental basins of the USSR. Sedimentation in modern basins). Izd. Akad. Nauk SSSR, 1954.
13. Troitskii, K. V. Primenenie Soosazhdeniya dlya Vydeleniya Sledov Razlichnykh Metallov (The use of co-precipitation in the isolation of traces of different metals). *Zh. Analit. Khim.*, XI, Vyp. 5, 1956.
14. Shchukarev, S. A. Sul'fidnye Vody SSSR (Sulfide waters of the USSR). Fiziko-Khimiya Mineral'nykh Vod i Lechebnykh Gryazei (Physical chemistry of mineral waters and curative muds). *Sb. st. Tsentr. Gos In-ta Kurortologii,* 1937.
15. Breger, I. A., M. Deul, and S. Rubinstein. Geochemistry and mineralogy of uraniferous lignite. *Econ. Geol.* 50, No. 2, 1955.
16. DeVore, G. The role of adsorption in the fractionation and distribution of the elements. *Journ. Geol.* 63, 159, 1955.
17. Deul, M., and C. S. Annel. The occurrence of minor elements in ash of low-rank coal from Texas, Colorado, North Dakota, and South Dakota. *U. S. Geol. Survey Bull.* 1036-H, 1956.
18. Goldschmidt, V. M. Geochemistry. Oxford, Clarendon Press, 1954.
19. Hammer, A. T. Adsorption of vanadium anions by hydrous oxides. *Ceramic Age,* 66, No. 3, 1955.
20. Krauskopf, K. B. Factors controlling the concentration of thirteen rare metals in sea water. *Geochim. et Cosmochim. Acta* 9, 1956.

Kuroda, P. K., and E. B. Sandell. Geochemistry of molybdenum. *Geochim. et Cosmochim. Acta,* 6, 35, 1954.

Lepp, H. The synthesis and probable geologic significance of melnikovite. *Econ. Geol.* 52, No. 5, 1957.

Lissner, A. Uber die Mineralstoffe der Braunkohlen. *Kl. Chem., Geol. und Biol.,* No. 1, 30, 1956.

Mellor, J. W. A. Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. XI (Cr, Mo, W). London, New York, Toronto, 1931.

Otte, H. U. Spurenelemente in einigen deutschen Steinkohlen. *Chem. Erde,* 16, 237, 1953.

Rankama, K., and T. G. Sahama. Geochemistry. Chicago, 1950.

Richard, C. E., H. T. Evans, Jr., and D. H. Richter. Smythite, a new iron sulfide, and associated pyrrhotite from Indiana. *Am. Mineral.,* 42, 309-333, 1957.

Rosenthal, G. Versuche zur Darstellung von Markasit, Pyrit und Magnetikies aus wassirigen Losungen, bei Zimmertemperatur. *Heidelberg. Beitr. Miner. u. Petrog.,* Bd. 5, H. 2, 146-164, 1956.

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SULFUR-BEARING APATITES

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Abstract

In analyzing numerous apatites from various deposits in the Soviet Union, the author has paid attention to the character of the isomorphous replacement between P, S, and Si. In contrast to ellestadite, in which every two P^{5+} atoms have been accordingly replaced by S^{6+} and Si^{4+}, in apatite from the Shishimsk mine the Si/S ratio = 1.34 : 1, i.e. an excess of Si not compensated by sulfur has been observed (Table 2), which in the author's opinion has been compensat by the replacement of the bivalent O^2 ion by a monovalent ion $(OH)^-$. In this case the isomorphous replacement may be expressed by the following schemes $2P^{5+} \rightarrow Si^{4+} S^{6+}$ and $(3P^{5+})O^{2+} \rightarrow (S^{6+} 2S^{4+})\ (OH)^-$.

In the apatite from the Madezhnoe deposit, in which P^{5+} has been replaced S^{6+}, and the composition corresponds to the formula $Na_6Ca_4S_6O_{24}Cl_2$, the isomorphous replacement corresponds to the scheme: $Ca^{2+} P^{5+} \rightarrow Na^+ S^{6+}$. The other apatites from the Aldan (deposit Leglier and Emeldzhak, Table 1) contai rare earths and Na along with S and Si. In apatites of such composition the following isomorphous replacement is possible:
$2Ca^{2+} \rightarrow Na^{1+} TR^{3+}$, $2P^{5+} \rightarrow S^{6+} Si^{4+}$; $Ca^{2+} P^{5+} \rightarrow TR^{3+} Si^{4+}$; $Ca^{2+}\ P^{5+} \rightarrow Na^{1+} S^{6+}$.
Data on specific gravity, refractive indices and lattice dimensions of apatites depending on the per cent of the S content in them have been compared in the article (Table 5).

Sulfur in minerals of the apatite group was discovered first by Rogers, in quantities up to 12% SO_3, in his analysis of a mineral from Crestmore, California; the mineral was named wilkeite [1].

R. Brauns [2] proved the presence of about 1% SO_3 in an apatite from the mine dumps at Laacher See. All three of Brauns' analyses, one of which is reproduced in Table 1, indicate an excess of calcium and a deficiency of the monovalent anions, in reference to the commo formula of apatite:

$$Ca_{10}P_6O_{24}(F,Cl,OH)_2 .$$

Silica was not included in the analysis, and the presence of sodium in his apatite was a surprise to Brauns. He suggested that SO_3 may be replacing F, Cl, OH, in the apatite structures and that the corresponding pure sulfate-apatite should be represented as $3Ca_3(PO_4)_2 \cdot CaSO_4$ containing 52.55% CaO, 39.95% P_2O_5, and 7.50% SO_3.

McConnell [3] and Ellestad discovered a new mineral, ellestadite, during their studies of the wilkeite from Crestmore. This new miner is markedly different from wilkeite in its composition and contains out 3% P_2O_5; the rest of the phosphorus has been replaced by sulfur id silicon. This places the mineral close to the end of the series. ne end-member of the series, according to McConnell, is represented the formula $Ca_{10}S_3Si_3O_{24}(F, Cl, OH)_2$ where every two atoms of P^{5+} e replaced correspondingly by S^{6+} and Si^{4+}. A replacement of this pe may be considered as proved and incontrovertible from the point view of crystal chemistry because the ionic radii of P^{5+}, S^{6+}, and $^{4+}$ are close to each other (0.35, 0.29, 0.39 Å respectively), because e total number of the ions in the lattice remains unchanged, and be- use the balance of positive and negative valencies remains undis- rbed.

One cannot fail to notice, on consideration of the analysis of wilke- , that Rogers shows no data on Cl or F, and that he finds only traces water, although his analysis sums to 100%. Consequently, doubt velops as to the reliability of his analysis. A. Eakle and A. Rogers] cite also two more incomplete analyses of wilkeite from the same cality in which there is considerable variation in P_2O_5, F, and Cl, ich has led McConnell [3] to his conclusion regarding the incon- ancy of the composition of wilkeite. It is extremely difficult to inter- et analyses of the test materials, especially when the analyses were ade more than 40 years ago. We are inclined to believe, neverthe- ss, that wilkeite and the subsequently discovered ellestadite probably ve the same chemical composition and that wilkeite is probably an termediate member of the ellestadite-apatite isomorphous series, ereas the presence of CO_2 in wilkeite probably results from admix- re of calcite, which is commonly associated with wilkeite.

There is a deficiency of the monovalent group in the ellestadite, cording to McConnell, as well as in Brauns' apatite from the Laacher e. Both of these authors explain this deficiency by the presence of e voelckerite molecule, $3Ca_3(PO_4)_2 \cdot CaO$, in their materials. Such planations are hardly acceptable, however, and the very existence of ch a molecule is now questioned by many authors, including the thor of this report [5]. The deficiency of the monovalent anions in lestadite and wilkeite may be accounted for, it appears, by inexact terminations, either of fluorine or of water.

The problem of mutually isomorphous replacements of P, S, and Si s been discussed on many occasions, both in our literature and road, with different authors arriving at different conclusions. Con- quently, attention was given to this problem in the analysis of many mples of apatite from various sources in the Union. The presence sulfur was proved by the author in the instance of three apatites om three different phlogopite deposits in the Aldan District and of e apatite from the Shishim Mine, Ural. Chemical analyses of the atite group of minerals and of the apatites proper in which sulfur is und are reported in Table 1.

The Shishim apatite had been analyzed by I. D. Borneman [6] in 38, but it was desirable to repeat her analysis in view of the

Table 1. Chemical Analysis of Apatites Containing Sulfur

Constituent	Wilkeite, Crestmore, California	Ellestadite Crestmore, California	Laacher See, Rhineland	Shishim Mine, Ural	Leglier, Aldan	Emeldzhak, Aldan	Na zh Al
P_2O_5	20.85	3.06	39.66	32.91	40.36	40.54	38
SiO_2	9.62	17.31	n.d.	3.77	0.47	0.40	ab
SO_3	12.28	20.69	1.30	3.74	0.53	0.36	2
CO_2	2.10	0.61	abs.	1.80	abs.	abs.	1
CaO	54.44	55.18	53.60	55.73	53.54	53.94	53.
SrO	n.d.*	n.d.	n.d.	0.10	n.d.	0.02	0.
Rare Earths	n.d.	n.d.	n.d.	abs.	2.05	1.29	tra
Fe_2O_3	n.d.	0.22	1.10	abs.	abs.	abs.	abs
Al_2O_3	n.d.	0.13	1.10	abs.	abs.	abs.	abs
MnO	0.77	0.01	n.d.	abs.	abs.	0.02	tra
MgO	n.d.	0.47	0.14	abs.	abs.	0.18	abs
K_2O	n.d.	n.d.	2.70	abs.	abs.	abs.	abs
Na_2O	n.d.	n.d.	2.70	abs.	0.35	0.16	0.
F	n.d.	0.57	0.93	abs.	2.56	1.80	0.
H_2O	trace	0.63	abs.	1.59	0.28	0.39	0
Cl	n.d.	1.64	0.42	0.62	0.81	2.10	3.
Insol. Residue	abs.	abs.	0.60	abs.	abs.	abs.	abs
Total	100.06	100.52	100.45	100.26	100.95	101.20	101.
$-O = F_2$	-	0.61	0.47	0.14	1.25	1.22	0.
Sum	100.06	99.91	99.98	100.12	99.70	99.98	100.
Sp. Gr.	3.234	3.068	3.20	3.113	3.209	3.193	3.1
Analyst	Eakle	Ellestad	Brauns	Vasileva			

*n.d. = not determined

somewhat unusual composition of the mineral. The two analyses of the Shishim apatite agree very well (Table 2) and may be accepted as reliable accordingly.

The only discrepancy between the two analyses is between the 0.78 F reported by Borneman and by the absence of fluorine reported in th later analysis. This may be ascribed to the error in the determinatio

Table 2. Chemical Analyses of Apatite from Shishim Mine

	Analysis by Z. V. Vasileva			Analysis by I. D. Borneman		
Constituent	Weight per cent	Atomic proportions	Atomic proportions without $CaCO_3$	Weight per cent	Atomic proportions	Atomic proportions without $CaCO_3$
P_2O_5	32.91	4637	4637	32.40	4563	4563
SiO_2	3.77	627	627 } 5731 = 6 × 955	3.56	593	593 } 5561 - 6 ×
SO_3	3.74	467	467	3.24	405	405
CO_2	1.80	409		2.05	466	-
CaO	55.73	9938	9529 9538 = 10 × 954	56.26	10046	9580
SrO	0.10	9	9	-	-	- } 9621 = 10 ×
MnO	not found	-		trace	-	-
K_2O	not found	-		0.07	15	15
Na_2O	not found	-		0.08	26	26
H_2O	1.59	1765	1765	1.38	1200	1200
F	not found	-	- } 1940 = 2 × 970	0.78	(411)	(411) } 1355 = 2 ×
Cl	0.62	175	175	0.55	155	155
$- O - Cl_2$	100.26 0.14			100.37 0.45		
Sum	100.12			99.92		
Sp. gr.	3.113			3.121		

fluorine. In the analysis done by the author, fluorine was deter- ined by the V. V. Danilova method, using the sulfuric acid solution; F could be detected in any of 10 successive fractions of the distil- te. Consequently, the report on fluorine in the more recent analysis ay be regarded as more reliable.

Colorless transparent crystals of apatite, 3 to 4 cm in size, in the ishim Mine, are found in the "nests" of calcite or as direct inclu- ons in the monticellite rock. The apatite here is apparently of con- ct metamorphic origin. Its refractive indices, measured by the mersion method with sodium light, are as follows: N_o = 1.652 ± 002; N_e = 1.647 ± 0.002; $N_o - N_e$ = 0.005. The parameters calcu- ted from the X-ray diffraction pattern are: a_o = 9.42 Å; c_o = 6.92 Å; /a = 0.734.

An appreciable content of CO_2 and an excess of calcium are shown both analyses. Microscopic studies of thin sections indicate the esence of the finest particles of calcite in the apatite, which cannot isolated from apatite either by the heavy-liquid separation or by nd-picking under a binocular lens. Computations from the analysis ove that the atomic quantities of CO_2 and of the excessive calcium e the same (409), and it is reasonable therefore to regard all of the rbonic acid as bound in the form of $CaCO_3$.

As already stated, the ratio of silicon to sulfur in ellestadite is 1:1. the other hand, the Si:S ratio is 1.34:1 in the Shishim apatite, i.e., e get the impression that the excess of silicon is unbalanced.

Studies by P. Dihn and R. Klement [4] dealing with the possibility the P, S, and Si isomorphism proved that apatites may depart from e ideal formula. Certain positions may be left vacant in the apatite ructure and also there may be excesses of certain ions in reference the $Me_{10}X_6O_{24}Y_2$ formula. This assumption is introduced in order account for valency compensations required in the case of excesses S or Si in the apatite. Dihn and Klement present characteristics of atites whose formulae deviate from the ideal on the basis of their perimental findings (Table 3) and show that a substance containing

Table 3

Data for Apatites Deviating from the Ideal Formula
$Me_{10}X_6O_{24}Y_2$ (According to Dihn and Klement)

Formula	a	c	c/a	G(calc.)	G(dtd.)
$_{.0}P_6O_{24}F_2$	9.36*	6.88*	0.732*	3.19*	3.20*
$_{0.5}SiP_5O_{24}F_2$	9.35	6.79	0.726	3.29	3.20
$_{.5}P_5SO_{24}F_2$	9.66	6.91	0.731	3.05	3.08
$_{0.5}Si_2P_3SO_{24}F_2$	9.40	6.81	0.724	3.23	3.20
$_{.5}SiP_3S_2O_{24}F_2$	9.46	6.91	0.731	3.04	3.10
$Ca_9SiP_4SO_{24}F_2$	9.39	6.89	0.734	3.24	3.10

ata from Mehmel

11 metallic ions may still fit into the apatite structure but that this number is the limit, since all attempts at producing an apatite with 12 or 13 metallic ions were unsuccessful. However, these authors based their conclusions entirely on the X-ray diffraction patterns of their synthetic products without adequate chemical analytical control for their purpose, in our opinion.

From the point of view of Dihn and Klement, by assumption that the presence of Si in the apatite may be compensated by an excess of Ca ions, there should be 0.90% more calcium to compensate the excess o silicon in the apatite from the Shishim Mine. This is not sustained by the analysis. For that reason, the suggestion of I. D. Borneman [6] regarding a replacement of the divalent O^{2-} ion by the monovalent OH ion, in the presence of an excess of Si, appears to be a more reliable one to us and, accordingly, the apatite from the Shishim Mine may be represented by the formula $Ca_{10}Si_{0.65}P_{4.85}S_{0.50}O_{23.85}OH_{2.15}$.

It may be evident therefore that isomorphous replacements in apatites may be represented by the following series, using the Shishim ellestadite and apatite as examples:

$$\text{(a)}\quad 2P^{5+} \leftarrow S^{6+}Si^{4+};$$

$$\text{(b)}\quad (3P^{5+})O^{2-} \leftarrow (S^{6+}2Si^{4+})OH^{-}.$$

Analysis of apatite from the phlogopite deposit at Nadezhnoe, Aldan suggests the possibility of still another course in the P^{5+} and S^{6+} isomorphous replacements. Analysis of this apatite and the appropriate recalculations are shown in Table 4.

The presence of sulfur is not associated with the presence of silic in this case, but the presence of a small amount of sodium is established by chemical analysis. Thus the simultaneous presence of Na a S in the apatite results in a mutual compensation of positive and negative valencies.

As already stated [7], the apatite from Nadezhnoe is an intergrowth, a pseudomorph of the Cl-OH apatite after the phosphorus-free Na-S-Cl apatite represented by the formula $Na_6Ca_4S_6O_{24}Cl_2$. Constitution of the Na-S-Cl apatite may be computed either from its sulfur

Table 4. Chemical Analysis of Apatite from Nadezhnoe

Constituent	% by Weight	Atomic proportion	Atomic proportion without $CaCO_3$		Na-S-Cl apatite $Na_6Ca_4S_6O_{24}Cl_2$ Atomic proportions	Cl-OH apatite $Ca_{10}P_6O_{23}(Cl,OH,F)_2$ Atomic proportions	
P_2O_5	38.63	5442	5442	5766 = 6 × 961	323 = 6 × 54	5442 =	6 × 907
SO_3	2.58	323	323				
CO_2	1.05	238					
CaO	53.23	9492	9254	9589 = 10 × 959	217 = 4 × 54	9034	9053 = 10 × 90
SrO	0.20	19	19			19	
Rare Earths	trace	—					
Na_2O	0.98	316	316		316 = 6 × 53		
H_2O	0.79	877	877	1916 = 2 × 958		877	1808 = 2 × 90
F	0.10	52	52			52	
Cl	3.50	987	987		108 = 2 × 54	859	

r from its sodium content. Our computation was based on sulfur, be- ause the analysis for sulfur was more exact than the analysis for sodium (sulfur was determined in duplicate), whereas there was a probability of errors in the sodium analysis. For that reason, we took 23, the atomic quantity of sulfur, as the basis for the allocation of the nalytical constituents to Na-S-Cl apatite or ordinary apatite.

It is difficult to imagine what would be the end-member of the iso- orphous series whose intermediate member is the Shishim apatite, lthough the suggestion of I. D. Borneman [6], to the effect that it may e a "silicon apatite," $Ca_{10}Si_6O_{18}(OH)_8$, is scarcely feasible. The resence of Si^{4+} in apatites is accompanied, as a rule, either by the resence of RE^{3+} or of S^{6+}, as is indicated by many analyses of natu- al apatites, both by the author and by others, as reported in the iterature.

In the specimen of apatite from Nadezhnoe isomorphous replace- ent can be represented by the following equation: $Ca^{2+}P^{5+} \leftarrow Na^{+}S^{6+}$. is highly probable that the apatite from Laacher See, in which Na d S are present according to Brauns, is an intermediate member of e isomorphous series:

$$Ca_{10}P_6O_{24}(OH, Cl, F)_2 - Na_6Ca_4S_6O_{24}(Cl, F)_2$$

Two of the other apatites from Aldan, from the Leglier and the meldzhak deposits, contain rare earths and sodium, as well as sulfur d silicon. There may be isomorphous replacements in apatites of ch composition:

$$2Ca^{2+} \leftarrow Na^{+}TR^{3+}; \quad 2P^{5+} \leftarrow S^{6+}Si^{4+};$$

$$Ca^{2+}P^{5+} \leftarrow TR^{3+}Si^{4+}; \quad Ca^{2+}P^{5+} \leftarrow Na^{1+}S^{6+}.$$

Calculations of either one of the analyses, with attention to isomor- ous replacements of the type here indicated, show that the results rrespond very well to the ideal formula $Me_{10}X_6O_{24}Y_2$.

Table 5 presents the data on specific gravity, refractive indices, d lattice parameters for the two apatites (examined by the author) in hich the highest amounts of sulfur were found, the Na-S-Cl apatite om Nadezhnoe and the apatite from Shishim Mountains. The data on e Cl-OH apatite which forms close intergrowth with the Na-S-Cl apa- e [7] are included (Table 5) for the sake of comparison.

Table 5. Specific Gravity, Refractive Indices, and Lattice Parameters of Sulfur-Bearing Apatites

Apatite and Source	% SO_3	Sp. Gr.	ω	ε	a_0	c_0	c_0 d_0
-S-Cl apatite; Nadezhnoe	50.80	2.93	—1.675—		9.56	6.77	0.708
atite; Shishim Mine	3.74	3.113	1.651	1.648	9.42	6.92	0.734
-OH apatite; Nadezhnoe	-	3.16	1.642	1.633	9.41	6.89	0.729

It is extremely difficult to correlate the presence of sulfur with th optical and the physical properties of apatites, because, as a rule, suc apatites also contain other elements affecting these properties. One may see, nevertheless, that the specific gravity of apatite is noticeabl lower in the presence of sulfur, whereas the refractive indices are higher and the double refraction is lower, to the point that apatite ma become practically isotropic at the maximum of the sulfur content (th Na-S-Cl apatite). The a_0 parameter of the crystal lattice becomes appreciably larger under such conditions.

REFERENCES

1. Eakle, A. S., and A. F. Rogers. *Amer. Journ. Sci.*, Ser. 4, 37, 262, 1914.
2. Brauns, R. *Neuss Jahrb. Min.*, Beil. B., 41, 60, 1917.
3. McConnell, D. *Amer. Mineral.*, 22, 977, 1937.
4. Dihn, P., and R. Klement. *Zeits. Elektrochem.*, 48, 331, 1942.
5. Vasileva, Z. V. *Zap. Vsesoy. Mineral.* (in press).
6. Borneman, I. D. *Doklady Akad. Nauk SSSR*, 19, 253, 1938.
7. Vasileva, Z. V., M. A. Litsarev, and N. I. Organova. *Doklady Akad. Nauk SSSR*, 118, 577, 1958.

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SOME DATA ON THE BORON CONTENT OF IGNEOUS ROCKS IN THE TURINSK ORE DISTRICT, URAL MOUNTAINS

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Abstract

Spectroscopic analysis of the boron content in igneous rock of the Turinsk
ral) copper district was performed on 16 pre-skarn pyroxene gabbros, gran-
iorites and diorites; 5 extrusive mafic porphyrites; and 5 post-skarn spes-
rtite lamprophyres. With two exceptions the pre-skarn intrusives ranged from
-30 ppm boron, about equal to the concentration of the post-skarn lampro-
yres and about that of the boron content of the extrusives. The overall boron
ncentration of the Turinsk igneous rocks is around three times the boron con-
nt of the average igneous rock. Boron analyses made on single mineral com-
nents of selected intrusive and extrusive rocks illustrate the marked concen-
ation of boron in plagioclase and not in hornblende or augite. No credence is
aced on early fixation of boron as datolite or axinite during crystallation of
afic and ultramafic rocks. This mineralization is thought to arise from later
drothermal action. A plot of the boron content in rocks compiled from several
vestigators points out the relative constancy of boron in mafic and silicic rocks
10 ppm) with a possible trend to a higher boron content in mafics and inter-
ediates than in silicics. The original boron content of a magma is decisive in
termining the extent of isomorphous substitution or boron mineralization
roughout the rock crystallization history.

Many investigators are now engaged in the problem of the distribu-
n of rare and dispersed elements in igneous rocks. It has been es-
blished that such elements are good indicators in rock and ore genesis
ocesses. These elements commonly permit us to ascertain the gene-
relationships of ore deposits with intrusions of different kinds.

There is a very limited body of data on boron in igneous rocks. We
ow only of studies by V. M. Goldschmidt and C. Peters [8], V. M.
ldschmidt [9], T. G. Sahama [14], S. Landergren [10], S. R. Nockolds
d R. L. Mitchell [12], S. R. Nockolds and R. Allen [13], B. Wasser-
ein [15], and P. H. Lundegårdh [11], which contain some interesting
ta on boron, chiefly in granites and mafic rocks. Data on boron in
ermediate rocks are not as abundant, however, and there are no data
boron in vein rocks.

Until recently there were no data on boron in rocks from different
gions of the Soviet Union. The reports by V. V. Melnitskii [6] on
ron in rocks of the Tagil-Kushva District and V. L. Barsukov and
E. Kurilchikova [2] on boron in serpentinites were published only
1957.

Realizing the scarcity of data on boron content of igneous rocks, particularly of rocks of the intermediate composition, one may reaso ably assume that the results presented here may be received with so interest, inasmuch as they supplement to some extent our knowledge geochemistry of dispersed boron.

Determinations of boron in rocks were conducted by spectrographi methods developed at the V. I. Vernadskii Memorial Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USS The excitation source was a DC arc between boron-free carbon electrodes operated at 300 v and 10 a. Twenty mg aliquots of samples we volatilized in an electrode cavity 4 mm deep and 3.5 mm in diameter. The arc gap was 5 mm. The spectrum was recorded photographicall by the ISP-22 quartz spectrograph, with the aid of a 3-lens condenser The films were the "line-reproducing iso-ortho-chromatic" 1.4 unit, GOST. Lines 2496.7 Å and 2497.7 Å, with the sensitivity of 0.002% an 0.001% respectively, were used in the analysis. The determinations were based primarily on the first line because a Fe line is imposed o the second one (2497.7 Å). Mixtures of boron-free "average" igneou rocks, with added amounts of borax, were used as standards. Reproducibility of results was within $\frac{1}{2}$ to $\frac{1}{3}$ order of magnitude.

The Turinsk Ore Deposit (Turinsk Mines) embraces a group of skarn copper deposits which was investigated in detail by D. S. Korzhinskii [5]. One of these deposits (Vadimo-Alexandrovskoe) contains considerable datolite mineralization, associated chiefly with skarnize parts of limestones interlayered with Middle Devonian hornfels, and more rarely, with garnet, garnet-wollastonite, and epidote skarns. In investigating this mineralization, the question regarding the original boron content of igneous rocks at the site naturally arose in view of the supposed genetic relationship between ores and igneous rocks. Fo sake of comparison, we analyzed some samples of rocks of other deposits in the same district and several samples of rocks outside the boundaries of the mineralized area.

Igneous rocks in the area are of Variscan age and are represented by extrusives and intrusives of intermediate and mafic composition. The extrusives include hornblende and augite porphyrites—small shee within the limestone bodies. They are dark gray, dense rocks with a fine-grained matrix and phenocrysts of plagioclase, hornblende, and augite. As a rule, the hornblende is green. The plagioclase is andesine (Ab_{65-68} An_{32-35}) and locally even more calcic. The intrusives are represented by gabbros, gabbro-diorites, quartz diorites, and by many kinds of dike rocks: diorite-porphyrites and lamprophyres. Tw small massifs forming the northern and eastern boundaries of the deposit are composed of gabbro and gabbro-diorites. The latter are melanocratic rocks consisting chiefly of augite and plagioclase (Ab_{48-62}). In places there is also hornblende after plagioclase. As a rule, proportions of plagioclase and dark minerals are about equal, although locally the dark mineral fraction may be as high as 70%.

uartz diorites are found more rarely; they are small sheet intrusions r stocks consisting chiefly of plagioclase (Ab_{68-70}) with subordinate uantities of hornblende and quartz. Vein rocks are pre- and post-karn. The pre-skarn group includes diorite-porphyrites whose dikes nd sheet intrusions cut through the limestones; their contacts with the mestones are skarnized. They are gray or pale gray rocks with large henocrysts of plagioclase and hornblende. They resemble extrusive orphyrites in their appearance and composition and it is very difficult t times to tell these two kinds of rock apart. D. S. Korzhinski [5] be-eves them to be co-magmatic formations. The post-skarn rocks orm dikes within steeply dipping fissures. They are the youngest of ike rocks, inasmuch as they cut through all others, including skarns. hey are represented by lamprophyres (chiefly spessartites) and, ore rarely, by diabase porphyrites.

The remarkable constancy of boron content of all intrusive rocks, .002 to 0.003% (Table 1) is very obvious. There are two exceptions: he granodiorite from the Auerbach showed no detectable boron, and a ample of quartz diorite from a massif 20 km north of the ore district howed boron one order of magnitude higher (i.e., 0.03%). In many stances boron is twice as high in the Vadimo-Alexandrovskoe extru-ves than in the intrusives. The post-skarn dike rocks (spessartites) ontain just as much boron as the pre-skarn intrusive rocks (Table 1).

All of these facts suggest that within this ore deposit the concentra-on of boron in the magma remained at a certain constant level through-ut the magmatic stage here discussed. The fact that boron is higher in xtrusives than in intrusives is very interesting. As we know, volcanism accompanied by expulsion of large quantities of gases, including B_2O_3, s is evidenced by the formation of sassolite. One would think that bo-on should be volatilized from the magma during extrusions, and that e magma should become impoverished in boron for that reason. How-ver, in intrusions, the environments should be conducive to the forma-on of boron minerals and to the isomorphous entry of boron into crys-l structures of rock-forming minerals.

In order to ascertain the forms of boron in the rocks, we collected d examined certain single-mineral fractions of the rocks (Table 2), be-ause no boron minerals whatsoever could be detected in thin sections.

The results in Table 2 show convincingly that boron is concentrated most entirely in plagioclase of the intrusives and in the fine-grained atrix of the extrusives in which plagioclase is again a major constitu-t. In most cases there is no boron in the dark minerals. The pos-bility of boron enrichment in plagioclase was first mentioned by L. Barsukov [1] who had also proved this possibility by crystal emistry.*

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this connection it is noteworthy to recalled the existence of a boron-albite, eedmergnerite, discovered by Charles Milton of the U.S. Geol. Survey in ter-estrial evaporite deposits of the Tertiary Green River formation, Green River, yoming. EWH

Table 1

Sample No.	Rock	Source	Weigh % Bor
	Intrusive and Vein Rocks; pre-skarn		
0167	Diorite-porphyrite	Vadimo-Alexandrovskoe; Borehole 525	0.00
0171	" "	Ditto	0.00
0490	" "	Ditto; Borehole 515	0.00
0526	" "	Ditto; Borehole 526	0.00
F-02	" "	Frolovskoe; Kirov Memorial Mine	0.00
H-3	Diorite-porphyrite	Nikitinskoe; "Nikitinskaya" Mine	0.00
U-770	Quartz diorite	Headwaters of Larkovka River	0.00
0226	" "	Vadimo-Alexandrovskoe; Borehole 525	0.00
F-01	" "	Frolovskoe; Kirov Memorial Mine	0.00
AU-17	Granodiorite	Auerbach Deposit, N. Oral	—
U-15	Quartz diorite	Headwaters of Larkovka River	0.00
U-41	" "	Ditto	0.03
U-151	Gabbro-porphyrite	Ditto	0.00
BA-0501	Gabbro	Vadimo-Alexandrovskoe; Borehole 585	0.00
BA-0510	Gabbro	Ditto	0.00
U-161	Pyroxenite	Headwaters of Larkovka River	0.00
	Extrusive Rocks		
018	Augite porphyrite	Vadimo-Alexandrovskoe; Borehole 525	0.00
080	Hornblende "	Ditto	0.00
0157	" "	Ditto	0.00
0344	" "	Ditto; Borehole 531	0.00
0464	" "	Ditto; Borehole 515	0.00
	Vein Rocks (Lamprophyres); post-skarn		
0161	Spessartite	Vadimo-Alexandrovskoe; Borehole 525	0.00
0447	"	Ditto; Borehole 505	0.00
0449	"	Ditto; Borehole 505	0.00
0512	"	Ditto; Borehole 526	0.00
0570	Spessartite (altered to some extent)	Ditto; Borehole 529	0.00

It is not possible therefore for us to agree with Sahama's [14] con-tention that boron accumulates mainly in dark minerals. Nor is it possible for us to agree that boron may be fixed in primary datolite and axinite in mafic and ultramafic rocks. No single investigator has thus far been successful in detecting these minerals as accessories in igneous rocks. A large number of observations prove that these minerals are formed in the post-magmatic stage of the process and with hydrothermal activity.

Until recently boron was generally believed to accumulate in the end-products of magmatic differentiation, in granites and pegmatites. This view was shared also by A. E. Fersman [7]. A. P. Vinogradov [3

Table 2. Boron Content in Weight Per Cent of Single-Mineral Fractions of Certain Rocks of the Turinsk Deposit

ample No.	Rock	Mineral			
		Hornblende	Augite	Plagioclase	Matrix
A-0501	Gabbro	—	abs.	0.01	—
A-0510	Gabbro-diorite	—	abs.	0.006	—
226	Quartz-diorite	abs.	—	0.008	—
-01	Ditto	abs.	—	0.002	—
171	Diorite-porphyrite	abs.	—	0.005	—
490	Ditto	0.002	—	0.008	—
18	Augite-porphyrite	—	0.002	—	0.02
80	Hornblende-porphyrite	0.002	—	—	0.005
157	Ditto	abs.	—	0.002	n.d.
464	Ditto	abs.	—	—	0.002

roved, however, that the boron averages are practically the same oth in mafic and in silicic rocks and that they amount to 1 x $10^{-3}\%$B see Fig. 1).

Figure 1 is a summary of many determinations of boron in rocks of ifferent kinds and an attempt at correlation of boron content with rock omposition. We do not consider here isolated data on ultramafic ocks. For mafic, intermediate, and silicic rocks, we note that most oints in the diagram fall very close to the averages. The average oron content will probably also be about 1 x $10^{-3}\%$ for intermediate ocks as is indicated by the plot. However, several points are very ar from the averages and represent boron anomalies 3 times and, for ome granites, even 5 and 10 times the average, because of enrichment f such granites in tourmaline [B. Wasserstein, 15]. The diagram also hows that there is more boron in mafic and intermediate rocks than in ilicic rocks in many cases. This generalization is supported by ockolds and Mitchell [12] in their studies of the Garabal Hill-Glen yne Complex. There boron content decreases in the series from yroxene-mica diorite to granodiorite.

The general impression from the foregoing considerations is that early everything depends on the original boron content of the magma rom which this or that kind of rock has been formed. In all probability if the original boron content is low, all of it isomorphously enters rystal structures of rock-forming minerals, particularly plagioclase structures in the case of mafic and intermediate rocks. The residual cidic solution is thereby impoverished with respect to boron. If the riginal boron content is high in the magma, the excess of boron which oes not isomorphously enter into rock-forming minerals remains in he residual solution (melt) and either contributes to the formation of ourmaline granites or passes into pegmatites in the course of differntiation. In some instances, however, boron-enrichment of the magna may be so great that the excess boron, migrating from the magmatic "hearth" in solution or gas, may under favorable condition give rise to large accumulations of tourmaline, axinite, datolite, and probably other boron minerals.

Thus boron "highs" in igneous rocks are among the factors conducive to the formation of boron deposits. And indeed, V. V. Melnitskii [6], as well as the author of this paper, in one of her earlier publications [4], had noted high concentrations of boron in igneous rocks neighboring boron deposits or where there were geochemical indications of boron minerals. The rocks we examined contain on the whole about three times the average boron content of igneous rocks. This is entirely reasonable, in view of the datolite mineralization at the Vadimo-Alexandrovskoe and at other localities within the Turinsk Ore Deposit.

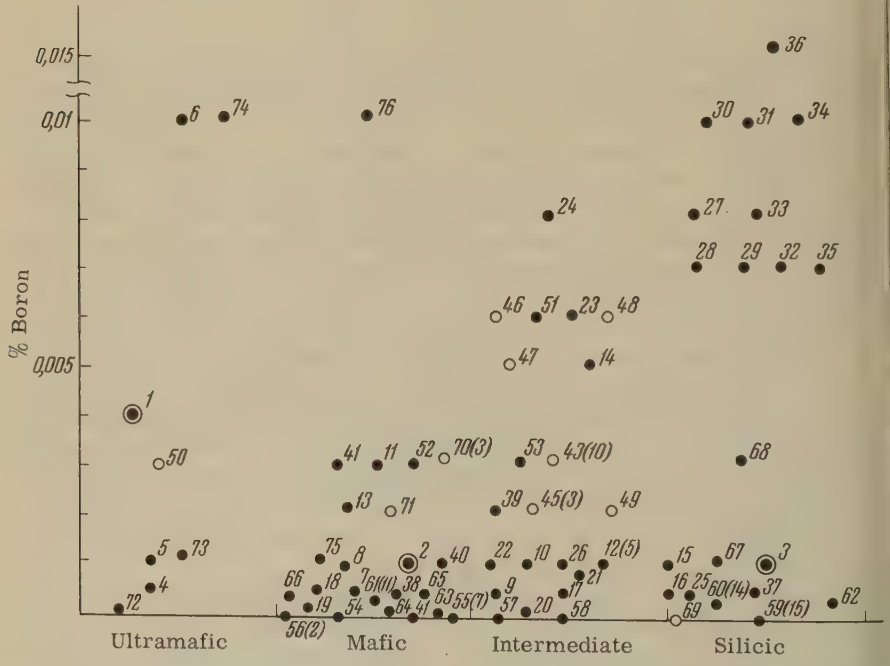

Fig. 1. Boron content of igneous rocks of different composition. ◉-Averages, according to A. P. Vinogradov; ○-our data; ●-data by other investigators. (Figures in parenthese show the number of analyses.)

(a) A. P. Vinogradov [3]: 1-average; 2-average; 3-average.

(b) V. V. Melnitskii [6]: 4-dunite, Ural; 5-pyroxenite, Ural; 6-pyroxenite, Ural; 7-gabbro, Ural; 8-gabbro, Ural.

(c) S. R. Nockolds and R. L. Mitchell [12]: 9-andesite, Hawaii; 10-andesit Hawaii; 11-norite, California, USA; 12-tonalite, California, USA; 13-gabbro, California, USA; 14-tonalite, California, USA; 15-granodiorite, California, USA; 16-granodiorite, California, USA; 17-tonalite, California, USA; 18-basalt, Lass Peak, USA; 19-olivine basalt, Lassen Peak, USA; 20-andesite, Lassen Peak, US

1-dacite, Lesser Antilles; 22-dacite, Lesser Antilles; 23-diorite, Scotland; 4-xenolithic diorite, Scotland; 25-granodiorite, Scotland; 26-dacite, Lesser ntilles; 54-hornblende gabbro, California, USA; 55-basalt and andesite, California, USA; 56-olivine basalt, California, USA; 57-tonalite, California, USA; 58-onalite, California, USA; 59-granites, USA, (15 analyses).

(d) B. Wasserstein [15]: 27-granite, S. Rhodesia; 28-granite, Nyassaland; 9-granite, Bushveldt; 30-granite, Bushveldt; 31-granite, Bushveldt; 32-granite, ushveldt; 33-granite, Capetown; 34-granite, Capetown; 35-granite, Capetown; 6-granite, Capetown.

(e) S. R. Nockolds and R. L. Mitchell [12] : 51-diorite, Scotland; 52-gabbro, cotland; 53-diorite, Scotland.

(f) T. G. Sahama [14] : 37-granite, Finland; 38-norite, Finland; 41-gabbro, inland; 42-gabbro, Finland.

(g) V. M. Goldschmidt and C. I. Peters [8], V. M. Goldschmidt [9]: 60-ranites, Germany (14 analyses); 61-gabbro, Germany (11 analyses); 62-basalt 2 analyses); 65-augite andesite, Italy; 66-hornblende andesite, Italy; 67-parite, Italy.

(h) P. H. Lundegardh [11]: 68-granite.

(i) V. L. Barsukov [1] : 39-diorite, Transbaikal; 40-gabbro, Gornaya horiya.

(j) V. L. Barsukov and G. E. Kurilchikova [2] : 72-dunite; 73-peridotite; 4-pyroxenite; 75-gabbro; 76-gabbro.

(k) Our Data: 43-quartz diorites, gabbros, gabbro-diorites, diorite-porhyries (average of 10 analyses); 44-quartz diorite; 45-quartz diorites, diorite-orphyrites (average of 3 analyses); 46-augite porphyrite; 47-hornblende porhyrite; 48-hornblende porphyrite; 49-hornblende porphyrite; 50-pyroxenite, steiskii Massif, N. Ural; 69-granodiorite, Auerbach Deposit, N. Ural; 70-spesartite (3 analyses); 71-spessartite.

REFERENCES

. Barsukov, V. L. Ob Izomorfizme Bora v Silikatakh (On the isomorphism of boron in silicates). (In press).

. Barsukov, V. L., and G. E. Kurilchikova. O Boronosnosti Serpentinitov (Boron in serpentinites). *Geokhimiya,* No. 5, 389-391, 1957.

. Vinogradov, A. P. Zakonomernosti v Raspredelenii Khimicheskikh Elementov v Zemnoi Kore (Regularity of distribution of chemical elements in the earth's crust). *Geokhimiya,* No. 1, 6-52, 1956.

. Getling, R. V. Datolit iz Izverzhennykh Porod Raiona d. Bodrak v Krymu i Nekotorye Geokhimicheskie Osobennosti Ego Genezisa (Datolite from igneous rocks of the Bodrak Village district, Crimea, and certain geochemical features of its origin). In press.

. Korzhinskii, D. S. Petrologiya Turinskikh (Skarn deposits of copper). *Trudy In-ta Geol. Nauk, Akad. Nauk SSSR,* Ser. Rudnykh Mestorozhdenii, Vyp. 68, 1948.

. Melnitskii, V. V. O Boroproyavlenii v Tagilo-Kushvinskom Raione Urala (Occurrences of boron in the Tagil-Kushva region of the Urals). *Proc. Acad. Sci. USSR,* Geol. Sci. Sec. (English trans.), Vol. 112, 73-75, 1957; *Doklady Akad. Nauk SSSR,* Vol. 112, 736-738.

. Fersman, A. E. Geokhimiya, T. 4, ONTI (Vol. 4, State Sci. Techn. Publ. Chem. Lit., Leningrad), 355 pp., 1939.

8. Goldschmidt, V. M., and C. Peters. Zur Geochemie des Bors. I. *Nachr. Ges. Wiss. Gottingen,* Math.-Phys. Kl. III. 25: IV: 27, 402-407, 1932.

8a. Goldschmidt, V. M., and C. Peters. Zur Geochemie des Bors. II. *Ibid.,* Math.-Phys. Kl. III. 28; IV: 31, 528-545.

9. Goldschmidt, V. M. Geochemistry. Clarendon Press, Oxford, 1954. 730 pp

10. Landergren, S. Contribution to the geochemistry of boron. II. Distribution of boron in some Swedish sediments, rocks, and iron ores. Boron cycle in the upper lithosphere. *Arkiv Kemi, Mineral, Geol.,* 19A, No. 26, 1945, 31 pp.

11. Lundegardh, P. H. Rock composition and development in central Roslagen, Sweden. *Arkiv Kemi, Mineral, Geol.,* 23A, No. 9, 1946. 160 pp.

12. Nockolds, S. R., and R. L. Mitchell. The geochemistry of some Caledonian Plutonic rocks: A study in the relationship between the major and trace elements of igneous rocks and their minerals. *Trans. Roy. Soc Edinburgh,* Vol. 61, Pt. 2, 533-575, 1948.

13. Nockolds, S. R., and R. Allen. The geochemistry of some igneous rock series. *Geochim. et Cosmochim. Acta,* Vol. 4, 105-142, 1953. Also The geochemistry of some igneous rocks series, Part II: *Ibid.,* Vol. 5, 245-285, 1954.

14. Sahama, Th. G. Spurenelemente der Gesteine im sudlichen Finnisch-Lapland. *Bull. Comm. Geol. Finlande,* No. 135, 5-86, 1945.

15. Wasserstein, B. South African granites and their boron content. *Geochim. et Cosmochim, Acta,* Vol. 1, 329-338, 1951.

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ON THE PRESENCE OF NIOBIUM AND TANTALUM IN MUSCOVITES FROM PEGMATITES OF THE DZIRULSK CRYSTALLINE MASSIF

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Abstract

The presence of a constant niobium and tantalum admixture as well as the xistence of small amounts of Be, Ca, Sn, Ti, V and W in muscovites from arious paragenetic complexes of pegmatite formations of the Dzirulsk massif as been established. The chemical and spectral study of muscovite specimens rom pegmatites of Karelia and the Ural Mountains has shown the presence of b in all investigated muscovites. The least content (0.003% of Nb_2O_5) has been ound in muscovites of pegmatites from Chupa (Karelia). The maximum conent (0.05% Nb_2O_5) proved to be in muscovites from pegmatites of the Dzirulsk nassif. Niobium and tantalum in muscovites are considered an isomorphous mpurity.

While studying relationships in the distribution of accessory rare lements in the Dzirulsk pegmatites in 1956-1957, the author had noted ne presence of niobium and tantalum, invariably as admixtures in nuscovites from paragenetically different pegmatitic complexes. In ddition to niobium and tantalum, small amounts of Be, Ga, Sn, Ti, V, nd W were found in the samples of muscovite.

In order to clear the problem as to the forms in which niobium and antalum are present in muscovites, samples of muscovite were hand icked most carefully under the binocular microscope. A careful exmination of the hand-picked sample under a polarizing microscope ailed to discover any foreign inclusions in muscovite. Moreover, it vas proved by optical studies that the muscovite in question is a prinary mineral. In order to isolate any possible inclusions of tantaloiobates that had escaped microscopic detection, the muscovite powder, fter its pulverization in an agate mortar, was centrifuged in Thoulet iquid (sp. gr. 3). The heavy liquid tests confirmed the complete abence of heavy mineral fractions in the test material. The light nineral fraction was analyzed chemically at the Ukrainian Giredmet aboratory, by Surichan, Pashkova, Pekarskaya, and other chemists. iobium was determined by the thiocyanate method (Alimarin's proceure, as modified by the Ukrainian Giredmet). Tantalum was deternined by the fluorene method (Nazarenko's procedure). As the result, developed that there is 0.05% Nb_2O_5 and 0.015% Ta_2O_5 in muscovites rom the pegmatites of the Dzirulsk Massif (Shroshi); these figures are verages of quadruplicate determinations.

Replicate control analysis of the Shroshi muscovite at the Laboratory of the Caucasian Institute of Mineral Raw Materials (KIMS) showed no departures from the results on Nb_2O_5 and Ta_2O_5 reported by the Ukrainian Giredmet.

There has arisen a reasonable question as to whether the presence of niobium and tantalum is characteristic only of the muscovites here tested or for others as well, in other pegmatitic fields of the USSR. To make this problem clearer, four samples of muscovite from Chupa, Karelia, and Kyshtym, Ural, were examined at the KIMS Laboratory for Nb_2O_5 and Ta_2O_5. The analyses, by T. G. Matsaberidze, were by the same procedures as previously stated. Prior to their chemical analysis, these muscovites were analyzed spectrographically at the KIMS and at the Georgian Geologic Administration laboratories. (N. F. Abashidze and M. R. Bendiashvili, Analysts.)

As the result of these studies, it was proved that 0.003 to 0.05% Nb_2O_5 is present in all of the muscovites from Karelia, Ural, and Dzirulsk and that the lowest Nb_2O_5, 0.003%, is characteristic of the Karelian muscovites. The Shroshi muscovites contain the highest amounts of Nb_2O_5, 0.05%, whereas the Kyshtym muscovites are intermediate between these two extremes (Table).

In addition to niobium and tantalum, Be, Ga, Ti, Sn, and V were found in all muscovites here examined. There is about 0.02% Ga in all; Be does not exceed 0.007%; Ti, Sn, V, W are present in amounts ranging from 0.01 to 0.1%. Curiously, the Nb/Ta ratio in the Shroshi muscovites is nearly the same as in the columbites from the Shroshi pegmatites and is practically 3. Comparisons of analyses of muscovites from the three pegmatitic provinces show that there is less niobium in the Karelian and in the Uralian muscovites than in the muscovite from the Dzirulsk.

Comparisons of the characteristic features of the pegmatitic fields whose muscovites were examined here indicate that niobium, tantalum, and beryllium minerals are not characteristic for the Chupa (Karelia) pegmatites [5, p. 514]. Indeed, these minerals are absent there, for all practical purposes. The insignificant amounts of niobium, tantalum, and beryllium in Karelian muscovites, as against the muscovites from Ural and Dzirulsk, appear to be due to their general deficiency in

Mineral and Source	%Nb_2O_5	%Ta_2O_5	Laboratory
Muscovite; pegmatites; Chupa, Karelia	0.003*		Caucasian Institute of Mineral Raw Materials
Muscovite; pegmatites; Kyshtym, Ural	0.02*	—	Caucasian Institute of Mineral Raw Materials
Muscovite; pegmatites; Shroshi (Dzirulsk)	0.05	0.015**	Ukrainian Giredmet and KIMS(i.e.CIMRM-VPS)

*Average of two analyses. **Average of four analyses.

that particular pegmatitic province. At the same time, the presence of the accessory columbite and beryl in the pegmatites of Dzirulsk (0.005 and 0.007% respectively), as isomorphous admixtures of niobium and beryllium in the muscovites, enables us to draw a preliminary conclusion to the effect that there exists a certain relationship in regard to the dependence between the amounts of the isomorphous admixtures of niobium, tantalum, and beryllium in muscovites and the concentrations of these elements in the magmatic solutions, as well as in regard to the geochemical environments of the formation of pegmatites. The practical absence of the minerals of these elements in the Chupa pegmatites tends to support our suggestion [5, p. 514]. Moreover, the very fact of the presence of Nb_2O_5 in the Chupa pegmatites, in such insignificant quantities as 0.003%, is probably an indication of the deficiency of niobium in the pegmatitic province in question, while, on the contrary, wherever columbite and beryl are present in pegmatites (Kyshtym and Shrosha) there are also high concentrations of the isomorphous niobium, tantalum, and beryllium in muscovites from the same pegmatites.

Our evidence permits us tentatively to regard niobium and tantalum as isomorphous admixtures in the muscovite structures.

It is known that isomorphous entries of elements into minerals are controlled by several factors among which the major ones are: a) size of ionic radii; b) valence; c) coordination number.

By consideration of the principal elemental constituents of muscovite, $KAl_2\ (AlSi_3O_{10})(OH)_2$, it is not too difficult to see that aluminum (ionic radius 0.57 Å) is the closest one to niobium, in respect to the size of its ionic radius. Neither potassium (ri = 1.33 Å) nor silicon (ri = 0.39 Å) is capable of being replaced by niobium whose ionic radius is 0.69 Å. In such manner, the supposition regarding the possible replacement of aluminum by niobium becomes most plausible, if we consider the size of the ionic radii of these two elements.

The six-fold coordination of niobium in silicates is scarcely to be doubted. Inasmuch as it is only aluminum, among the cations of the radical, that has six-fold coordination, it may be assumed rationally that it is the aluminum cation, in its octahedral coordination, that becomes replaceable by niobium in the muscovite structures here discussed.

Nevertheless, the replacement of aluminum by niobium is feasible only on a limited scale, inasmuch as the ionic radius of niobium is still too different from the ionic radius of aluminum by about 20% which is greater than the 15% allowed by Fersman's Rule (also known as Goldschmidt's Rule) governing isomorphous replacements [4, p. 370]. This excess may be compensated, however, as we shall presently see, summarily by a thermodynamic gain due to the higher charge of Nb^{5+} than of Al^{3+} which is replaced by niobium. The possibility of such replacement is sustained theoretically by the similarity between niobium and aluminum in regard to their electro-negativity (the "E" of Nb and Al is 220 and 240 kilo-calories respectively) [2]. It is worth remembering also that Al is a member of the characteristically diagonal isomorphous series: Ti-Nb-W [3].

Electrostatic compensation is a major factor playing an exceptiona role in heterovalent replacements. In this particular case two additional charges are introduced into the muscovite lattice in the replacement of Al^{3+} by Nb^{5+}. In this particular case, the electrostatic compensation is made effective apparently by the simultaneous entry of Be^{2+} into the muscovite lattice, in the substitution of Be^{2+} for Si^{4+}.

The presence of 0.007% beryllium, alongside niobium, was established spectrographically in the muscovites here investigated. The presence of beryllium in muscovites acquires a particular significance, in relation to the electrostatic compensation in the replacement of aluminum by niobium. The research of Beus [1] showed that the identical coordination numbers of beryllium and silicon, with respect to oxygen, and the similar ionic radii of Be^{2+} and Si^{4+} (0.34 and 0.39 Å respectively), as well as of the ionic radii of BeO_4^{6-} and SiO_4^{4-} are the determinants of the entry of beryllium into the silicate structures, by replacement of the silica tetrahedra by the beryllium-oxygen tetrahedra.

Moreover, the entry of beryllium into silicate structures (into the muscovite structure, in our case) is determined significantly by the presence or by the absence of free high-valency ions, at the time of the formation of minerals, by which the isomorphous substitution of Be^{2+} for Si^{4+} could be compensated.

The role of the high-valence cation is played by niobium, in this particular case. The course of the isomorphism may be represented as follows: While Be^{2+} is replacing Si^{4+}, the two missing charges are being compensated by a concurrent replacement of Al^{3+} by Nb^{5+}. The replacement is accompanied by a total thermodynamic gain as follows:

$$\text{EK } Be^{2+} + \text{EK } Nb^{5+} > \text{EK } Al^{3+} + \text{EK } Si^{4+};$$

$$2.65 + 13.50 = 16.25 > 4.95 + 8.60 = 13.55.$$

In concluding this discussion of certain major factors determining the isomorphous entry of niobium into the crystal lattice of muscovite, one may not refrain from observing that the attempt at outlining the course of the limited aluminum-niobium isomorphism, with the muscovites from the Shroshi pegmatites as the example, may be one of the possible solutions of the problem.

REFERENCES

1. Beus, A. A. Geokhimiya Berilliya (Geochemistry of beryllium). *Geokhimiya*, No. 5, 1956.
2. Povarennykh, A. *Zap. Vseso. Mineralog. Obshch.*, Ser. 2, Vyp. 84, 1955.

Shcherbina, V. V. Geokhimicheskie Osobennosti Ryada Periodicheskoi Sistemy (Geochemical characteristics of the diagonal sequence of elements in the Periodic Table). *Doklady Akad. Nauk SSSR*, 85, No. 4, 1952.

Fersman, A. E. Geokhimiya, T. 111, *ONTI*, 1937.

Fersman, A. E. Pegmatity. T. I., *Izd. Akad. Nauk SSSR*, 1932.

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ON THE FORMS OF GERMANIUM IN COAL

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Abstract

The results permit the conclusion that germanium is contained in two forr in the investigated coals: 1) a form related to the organic coal mass, as humacites of germanium, and 2) a form related to the mineral part of the coa To the first form may belong the germanium amount taken into solution togeth with humic acids. In this sense a comparison of data on the forms of german content in ordinary brown coal and in its concentrate is very significant. Sim taneously with the coal enrichment, an enrichment of the concentrate by the organic form of the germanium content from 83.3% to 97.3% has occurred.

Geochemical studies of relationships in the distribution of german um in coals have been conducted by the authors of this report since 1955.

A relationship has been established between germanium content an the coalification of plant substances (the coal formers) in the peat sta as well as between germanium and the nutritive-environmental substrata of the progenitors of coal.

Depending on the quantities of germanium present, the varieties o coal may be arranged in the following series: clarain; duro-clarain; claro-durain; durain with humified stem fragments (vitrain); durain; sapropel; and fusain. There is practically no germanium in fusain.

There is no unanimous opinion at present regarding forms and con pounds of germanium in coal. There is also no evidence in the litera ture of any attempt at an experimental approach to the solution of the problem. There is a widely held view that germanium replaces the hydrogens of carboxyl groups of humic acids to form germanium humates in coals; subordinate amounts of germanium silicates, german ates, or silico-germanates may also be present [1]. This view is ba on the fact that germanium may be extracted by alkalies, along with humic acids, in the treatment of brown coal. An indirect indication o the association of germanium with the organic constituents of coal is the fact that the bulk of germanium is found in the ash of the lighter fraction obtained by the heavy-liquid separation [2]. On the other han quantitative results for germanium are always too low for coal or coa ash prepared for analysis without the use of hydrofluoric acid, that is by the "soft" incineration (at temperatures not over 500°C).

The present article is our report on defining the character and the forms of germanium in coal. We used the following test materials:

own coal; its dull and vitreous varieties (durain and vitrain, respec-
ely); brown coal concentrate; hard coals: gas and coking coals.
eir characteristics are given in Table 1.

Table 1. Characteristics of Samples of Original Coal

Coal	% Bitumen "A"	% Humic acids	% Mineral admixtures	% Carboids by dif.	% Ge in coal ash
own coal, ordinary	1.34	35.7	19.05	43.91	0.00666
rain from same coal	2.27	39.0	7.6	51.13	0.0100
rain " " "	3.1	28.2	8.2	60.5	0.0016
own coal concentrate	2.7	64.3	12.1	20.9	0.016
s coal	3.3	abs.	11.9	—	0.0125
ne, after oxidation by $_2O_2$	3.1	51.0	—	—	—
king coal	1.4	abs.	5.36	—	0.0100
ne, after oxidation by $_2O_2$	1.3	abs.	—	—	—

Bitumens were determined by Soxhlet extraction of coal with an ohol-benzene mixture. After the extraction of Bitumen "A", the l residue was gently boiled with successive portions of 1% sodium droxide for 6 hours treatment [3] in order to extract humic acids. e extracted material was separated from the alkali by centrifuging 25,000 r.p.m. for 10 minutes. The alkaline treatment was carried . in the presence of hydrogen peroxide in the case of coals containing alkali-soluble humic acids.

Dynamics of the extractions and their efficiency in the isolation of nic acids are illustrated in Table 2. The determinations of

Table 2. Extraction of Germanium Together with Humic Acids

ple	Germanium in sample, gammas	Yield of Germanium with Humate Fractions												Total germanium extracted % of original Ge
		Humates I		Humates II		Humates III		Humates IV		Humates V		Humates VI		
		gammas	%*	gammas	%*	gammas	%*	gammas	%*	gammas	%*	gammas	%*	
n coal	266.4	60.2	28.4	79.0	36.5	41.0	19.2	33.0	15.5	10.0	4.7	—	—	83.3
in from e coal	174.0†	137.0†	100	—	—	—	—	—	—	—	—	—	—	79.0
n coal entrate	459.4	230	51.3	120	24.9	72.0	15.7	21.6	4.7	15.8	3.4	—	—	97.3
oal, af- xida- by H_2O_2	223.0	14.6	6.5	52.4	23.3	65.2	29.2	36.1	16.4	23.3	10.6	3.0	1.2	87.2

arently a misprint. % of total Ge in the original coal is probably meant.
se columns show percentages as of total germanium extracted.
here is no further extraction of Ge in the subsequent fractions. VPS

germanium were colorimetric using the phenylfluorone method deve oped by the GIREDMET.*

The results show, on the whole, that the extraction of germanium the alkali comes to an end after the 5th or 6th successive treatment. The lustrous variety of the coal is a special case, with all of its extractable germanium being removed in the very first treatment. Cu ously, the rate of extraction of germanium from different kinds of co parallels the proportions of their lustrous components as illustrated by the comparisons of Table 3. Thus, the rate of extraction of germanium increases with the increase in the vitrain content of the coal

Table 3. Rate of Extraction of Germanium as Influenced by Vitrain Content of Co

Coal Sample	% Lustrous varieties	% Ge extractabl after extraction
Vitrain	100.0	100.0
Brown coal, ordinary	15.0	28.4
Concentrate of ordinary brown coal	65.0	51.3

The balance sheet for the alkaline treatments of the coal with respect to germanium and to the coal is shown in Table 4.

It is evident from these results that the amounts of extractable humic acid and the proportions of extractable germanium show parall increases and that the peak of extractable germanium, 97.3% of the to germanium, is attained in the instance of the brown coal concentrate.

It would seem that this fact by itself is sufficient to confirm the hypothesis that the bulk of germanium in coal is tied up with the humi acid molecules. However, considering the amphoteric properties of germanium, it is equally possible that the passage of germanium into

Table 4. The Balance in the Extraction of Humic Acids and Germanium from Coal

Coal Sample	% of Coal Substance				% of Germanium		
	Yield of soluble humic acids	Coal residue	Dissolved mineral admixtures	Losses and unbalance	In coal residue	Extracted with humic acids	Unbalanc
Brown coal, ordinary	35.7	46.8	10.5	-7.0	16.2	83.3	-0.5
Vitrain from some coal	39.0	57.5	7.0	+3.5	29.7	79.0	+8.7
Durain from some coal	28.2	—	—	—	—	55.2	—
Brown coal concentrate	64.3	19.0	9.4	-7.3	12.8	97.3	+11.4
Gas coal after oxidation	51.6	43.7	4.64	-0.6	7.5	87.2	-5.3
Coking coal after oxidation	0.0	97.0	3.4	+0.4	100.0	0.0	—

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*"Gosudarstvennyi Institut Redkikh Metallov", "The Government Institute of Rare Metals".

e humic acid extracts is related simply to its possible direct solu- lity in the alkali by the formation of sodium germanate from germa- um bound in the mineral fraction of the coal.

In order to examine this possibility, a sample of the ash of the own coal containing 0.00615% germanium was treated with 1% sodium droxide at about the same temperature as was maintained in the ex- actions of humic acids. As the result of this treatment, the concen- ation of germanium in the ash dropped to 0.0038%. It should be noted at the decrease in the concentration of germanium in the coal ash om 0.0066% to 0.0025% as the result of the alkaline treatment of the iginal coal, and the decrease of its concentration in the coal ash from 00615% to 0.0038% as the result of the alkali treatment of the ash are the same order of magnitude.

Our experimental results also permit examination of germanate as e possible carrier of germanium in the extraction of germanium from al by alkali. The results presented in Table 5 may provide a partial swer to this problem in the case of hard coal. The two types of hard al (gas and coking) contain no alkali-soluble substances originally d yield no soluble germanium on treatment with alkali. After pre- eatment with hydrogen peroxide, however, one of these coals (gas) elded more than 50% of alkali-soluble acid products (based on origi- l weight). The sample of coking coal yielded no alkali-soluble oxida- n products under conditions of the test. It should be noted at the me time that there is a better chance for a germanate (Ge^{4+}) to pass o the solution [4]. We know that germanates, Me_2GeO_3 or Me_4GeO_4, rresponding to acids of the H_2GeO_3 and the H_4GeO_4 types, are easily med by interactions of the alkalies and the aqueous extracts, where- transfers of metallic germanium or of germanium oxides into their luble states require drastic pre-treatments including fusions with kalies. Consequently, the fact that no germanates are produced even er drastic oxidation of the coal, which ought beyond any doubt to lead the transition from Ge^{2+} to Ge^{4+} and to the subsequent extraction of

Table 5. Solubility of Germanium as Influenced by Solubility of Humic Acids of Coal

	Coal	
	Coking	Gas
ermanium in ash of original coal	0.010	0.0126
ne, after treatment of coal by alkali	0.010	0.0126
mic acids formed by the oxidation, % of original oal, by weight	0.0	51.6
ermanium in coal ash after the alkali treatment	0.010	0.00155
rmanium in the alkaline extract, % of the riginal coal in ash*	0.0	87.2

pparently a misprint. % of total Ge in the original coal is probably meant.

Ge^{4+} by the alkali, shows that germanium in the soluble humic acid fraction of the coal is bound in the organic constituents of the coal. appears, therefore, that the alkali-insoluble fraction of germanium i associated with mineral constituents of the coal in the form of a silico-germanate complex with some highly involved structures.

It is possible to conclude, therefore, that germanium is present in two forms in the coals we have examined: a) as germanium humates bound in the organic substance of the coal; b) in forms bound with the mineral substance of the coal. The first one of these includes germanium which is soluble together with humic acids. Examples of the distribution of germanium between the organic and the mineral fractions are presented in Table 6. A comparison between ordinary brow coal and the concentrate of the same coal is especially interesting wi regard to the proportions of germanium. The enrichment of brown coal in the concentrate is accompanied by an enrichment of germaniu in the organic fraction: from 83.3% in the original coal to 97.3% in th concentrate.

A comparison between the lustrous and the dull varieties of coal is also significant. Inasmuch as their ash contents are about the same, the mineral forms of germanium are more than twice as high in the dull as in the lustrous material; this may be explained by differences in the early stages of their coalification environments.

Table 6. Forms of Germanium in Coal

Coal	% of Total Germanium	
	As Ge humate in the organic fraction	As silicogermana or germanate in t mineral fraction
Brown coal, ordinary	83.3	16.7
Vitrain	79.0	21.0
Durain	55.2	44.8
Concentrate of brown coal	97.3	2.7
Gas coal	87.2	12.8

REFERENCES

Kirkby, W. A. *Fuel*, No. 3, 1950.

Kunstmann, F. H., and J. C. Hammersma. *J. Chem. Met. Min. Soc. South Africa*, 56, No. 1, 11, 1955.

Kukharenko, T. A. *Trudy Inst. Gor. Iskop. Akad. Nauk SSSR*, 2, 193-207, 1950.

Dzonson (Johnson?). *Uspekhi Khimii*, Vyp. 1, 1956. Gastinger, E. *Fortschr. chem. Forschung*, 3, No. 3, 603, 1955.

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GERMANIUM IN MINE WATERS OF THE KIZELOV COAL BASIN

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Abstract

The average germanium content in pit waters of the Kizelov coal field has been determined: it equals 1.5 mg/m^3. The water pumped out from 40 pits p ably carries out about 200 kg of germanium per year. The comparison with t germanium amount being yearly carried out with the coal bears witness to a strong bond of germanium with organic coal matter.

There are only limited indications in the literature on the content germanium in waters, and there is an apparent absence of data on ge manium in waters from coal mines.

In the Kizelov Basin, the Viseian Coal Measure lies between Devo an and Carboniferous limestones and is represented by sandy-clayey sediments containing more than 20 layers of coal. Hydrologic enviro ments of the Basin are very complex [3]. There are two basic types underground waters: the bed-fissure waters of the Coal Measure and waters in the carbonate sediments. Waters of the coal mines consist both of these types. As a rule, they contain free sulfuric acid in concentrations up to several thousand milligrams per liter.

Pumped waters from 20 coal mines in different parts of the Basin were tested in July 1957. The in-flow of acid to nearly neutral water is highly variable in individual mines. Moreover, there were also tests of waters from the limestones overlying the coal measures (Borehole 469). One sample of ground water was collected outside th boundaries of the mining area.

Water pumped from the Serov Mine was tested three times: in August 1956 and in July and August 1957. The results were the same in all three tests, and our data on germanium in these waters could n be accidental.

The phenylfluoron colorimetric method was employed in testing fo germanium [4] in mine waters. In order to isolate germanium from the interfering elements, following neutralization and evaporation of sample, germanium was extracted by carbon tetrachloride from the HCl solution of the residue [2].

Germanium was discovered in 13 out of 20 mine shaft waters (see table) brought up by the pumps, in concentrations up to 3 mg per cub meter or 2 to 6 times the limit of detection of Ge by the colorimetric method.

Germanium Content of Waters in Kizelov Basin

ource	Coal seams exploited	Free H_2SO_4, mg/liter	Discharge, m^3/hour	Germanium, mg/m^3
es:				
. Lenin	9, 11, 13	220.5	960	3
nsomolets	11	1362.2	96	1
odarskii	9, 11, 13	3694.6	174	1.5
6, Kapitalnaya	9, 11, 13	187.5	1850	1
dimirskaya	11	83.3	90	Not detected
41	11	Not detected	365	Not detected
44	11	Not detected	180	2
ov	11	426.3	50	3
in	11, 13	759.6	650	3
skii	11, 13	2597.0	360	3
nin	11, 13	1347.0	550	2
elyanka	11	553.7	120	1
38	9, 11, 13	735.0	246	Not detected
	9, 11, 13	764.4	300	Not detected
Kapitalnaya	9, 11, 13	568.4	850	1
	11 + 13	—	250	Not detected
	10, 11 + 13	—	60	Not detected
	9, 11 + 13	—	200	Not detected
	9, 11 + 13	—	150	2
	9, 11 + 13	—	80	1
ehole 469	—	—	—	Not detected
l in the yard of ouse No. 3, Krasin reet	—	—	—	Not detected

Such concentrations of germanium are 30 times as high as its con- tration in sea water [5] and nearly 17 times its concentrations in eral springs, as reported by V. I. Vernadskii [1]. No germanium s detected, however, in waters from Borehole 469 which drains the eian limestones overlying the coal measure or in water from a well ated outside the mining area. Consequently, it is reasonable to pose the Kizelov Basin waters are enriched by germanium which is ched chiefly out of coal.

Simplest calculations show that mine waters of the Kizelov Basin tain, on the average, 1.5 mg germanium per cubic meter and that ut 100 kg germanium is pumped out with the waters of 20 coal es annually. The total number of coal mines in the district is 40. uming that the content of germanium in all coal mine waters is as nd in the 20 mines we tested and assuming the pumping discharge m 40 mines to be about twice the discharge of the 20, the total germanium yielded in mine waters of the district should be about 20 kg annually. There is no doubt that germanium was being leached ou of coals prior to the opening of the district for exploitation, and is being leached even now from the places in the district where there i no mining at this time. We may believe, therefore, that total germa um leached out of the coals annually is somewhat higher still and tha the leaching of germanium out of the coals during the geologic time may have a substantial geochemical significance.

About 11 million tons of coal is mined in the Basin every year [3 containing probably several tons of germanium. A comparison of thi figure with the amounts of germanium discharged annually in mine waters shows that the scale of the leaching of germanium is modest and is in harmony with the data on the tenacity of the binding of germanium by the organic substance in coal.

Mine waters are formed differently in different coal mines and there are differences in the resistance of coals to weathering. Henc the differences in the rates of leaching of germanium out of coals. I is possible to suggest therefore that further studies of germanium in coal mine waters may result in discoveries of such sources of the metal that its economic production shall become feasible in the nearest future.

REFERENCES

1. Vernadskii, V. I. Istoriya Mineralov Zemnoi Kory (History of Minerals of the Earth's Crust). T. 11, ch. 1, Vyp. 11 and 111. ONTI, Leningrad, 1934 and 1936.
2. Hillebrand, V. F., G. E. Lundell, G. A. Bright, and D. I. Hoffman. Prakticheskoe Rukovodstvo po Neorganicheskomu Analizu (Practical Manual of Inorganic Analysis). Gos. Nauchni-Tekh. Izd. Khim. Lit., Moscow, 1957.
3. Pakhomov, I. V. Geologicheskaya Izuchennost' i Perspektivy Razvitiya Kizelovskogo Basseina (The state of geologic knowledge and possibilities of development of the Kizelov Basin). *Bull. Gorn. Obshch.* No. 2, Sverdlovsk, 1957.
4. Cluley, H. I. The determination of germanium. *Analyst,* 76, 1951.
5. Goldschmidt, V. M. Geochemistry. Oxford, 1954.
6. Ikeda. Germanii v Goryachikh Istochnikakh Beppu (Germanium in the Beppu hot springs). *Geologiya, Ref. Zhurnal,* No. 10, 1956.

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THE GERMANIUM CONTENT OF SOME SPRING WATERS IN KAMCHATKA

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Abstract

The germanium contents in waters of some springs of Kamchatka have been ermined. The amounts found range from 1 to 25 micrograms per liter. ides germanium, considerable amounts of boric acid and arsenic have been ected. An interdependence between an increase of the germanium content the rise of the water temperature is outlined.

Mineral springs of Kamchatka and of the Kurile Islands have been died systematically in recent years by members of the Expedition, 11th District, the Fifth Geologic Administration. Some of the ing waters were examined for germanium. Preliminary results presently to be discussed.

Germanium was determined colorimetrically, with the aid of phenyl- ron. Collection of germanium from the water and its separation m the interfering constituents were done as follows: germanium was lected by the Cl-anionite EDE-10 and was desorbed from the anion- by 9N hydrochloric acid by carbon tetrachloride and re-extracted 5 to 10 mls distilled water. This extract was the test solution for determination of germanium. The method was sufficiently sensitive the determination of 0.5 to 1 micrograms Ge per liter.

The springs here examined may be divided into several groups, de- ding on their geologic environments and the origins of their solutes. largest one, the Nalychevskaya Group, is situated at the headwaters he river of the same name on the eastern slope of the Valaginsk ge and it includes both the Nalychevsk and the Talovyi springs. The khkui springs, in the Kekhkui River valley, may also be referred to foregoing group on the basis of their geologic and hydro-chemical ironments.

The regional geologic environments of the group are defined by the ensive development of strongly folded Tertiary andesitic tuff- ccias locally ruptured by small Neogene granitoid bodies. At the e of the folded rocks, there is a complex of terrigenic sediments ch crop out somewhat farther north, in the Bogachev and Kronotsk tricts. The tuff-breccias are overlain by Quaternary effusives ch form a relatively severely dissected plateau.

Nalychevskii, Talovyi, and Kekhkuiskii springs, combined here into Nalychevsk Group, are thermal and their chemical composition is about the same, as is evident from the data in the table. Their wate are of the sodium chloride type containing 1.5 to 8 micrograms germanium per liter. Their boric acid and hydro-arsenate are conspic ously high. Bromine, iodine, and small amounts of naphthene acids are also present. The gaseous phase is chiefly carbon dioxide; nitro gen is predominant in the Talovyi spring. Curiously, germanium co tent of these three springs increases in parallel with both boron and temperature.

There are certain similarities in the geologic environments in the areas of the outcrops of the Karym and the Akademiya Nauk springs which are not far from the now active Karym Volcano, whose base is composed of Tertiary tuffogenic-effusive materials overlain by Quaternary effusives. The northernmost spring of the group, the Karymskii, carries 3 micrograms per liter of germanium. This spring is directly in the caldera of the volcano of the same name.

The Akademiya Nauk spring is at the southern extremity of the Karym Lake filling the extensive ancient caldera of the Karym Volcano. This spring carries the maximum of germanium: 25 micrograms per liter.

Despite the resemblances between the environment of their outcrops, the springs differ among themselves in their composition. Th Akademiya Nauk spring is of the sodium chloride type and is relative high in fluoride, while the Karymskii spring discharges water of a mixed composition in which magnesium bicarbonate is predominant.

The Uzonskii springs yield a special type of volcanic mineral water which is related directly to activities of the fumaroles. These springs are in the bottom of a large annular depression in the Tertiary and Quaternary volcanic materials composing an ancient caldera of the Uzon Volcano, according to B. I. Piip. One may observe outcrops of fumarole streams over the extensive area of this depression the fumaroles are concentrated within several fumarole fields. The Uzon mineral waters are formed by the action of volcanic exhalations on the fresh waters of the ground. As is characteristic for waters of such type, the Uzon waters are chiefly of the sulfate or the sulfate-chloride composition and are highly variable with respect to their cations. Germanium in the Uzon spring amounts to 8 micrograms pe liter.

The Savanskii mineral springs are in the south of Kamchatka. The are associated with the eastern apron of the West-Kamchatka Artesia Basin, which is composed of Neogene sediments overlain by a mantle of Quaternary effusions. The Upper Miocene sediments are exposed directly next to the spring whose outcrop is controlled by a N - S tectonic zone traceable for more than 2.5 km. The water is of the sodiu chloride type; the mineralization is relatively weak; 20 micrograms per liter of germanium is present.

It is a matter of considerable interest that the Savanskii thermal waters are directly associated with outcrops of petroleum and metha

Analysis of Kamchatka Springs

Spring	Ge, micrograms per liter	Temperature °C	pH	"Formula of Water" (according to Kurlov)
hevskii	8	73	7.1	$(CO_2)M_{4.2}\,\frac{Cl_{71}SO^{4}_{15}}{Na_{69}Ca_{20}}\,F_{0.7}\,HBO^{2}_{278}\,HAsO^{4}_{6}\,I_{0.8}\,Br_5$
yi	3	29.9	6.7	$(N_2)M_{5.6}\,\frac{Cl_{64}SO^{4}_{27}}{Na_{60}Ca_{38}}\,F_{0.7}\,HBO^{2}_{181}\,HAsO^{4}_{1}\,Br_1$
kuiskii	1.5	22	6.5	$(CO_2)M_{4.0}\,\frac{Cl_{56}HCO^{3}_{36}}{Na_{78}Ca_{14}}\,F_{0.4}\,HBO^{2}_{129}\,HAsO^{4}_{0.005}\,I_{0.6}\,Br_3$
nskii	3	37.5	6.5	$(CO_2)M_{1.5}\,\frac{HCO^{3}_{53}\,Cl_{41}}{Mg_{55}Ca_{27}}\,F_{0.6}\,HBO^{2}_{6}\,HAsO^{4}_{0.02}$
emii k SSSR	25	97	7.8	$(N_2)M_{0.84}\,\frac{Cl_{74}\,HCO^{3}_{15}}{Na_{96}}\,F_{1.4}\,HBO^{2}_{13}\,HAsO^{4}_{1}$
skii	8	76	5.8	$(CO_2)M_{0.6}\,\frac{Cl_{52}SO^{4}_{34}}{Na_{77}\,Ca_{15}}\,F_{0.5}\,HBO^{2}_{18}\,HAsO^{4}_{0.1}$
skii	20	75	7.4	$(CH_4)M_{0.8}\,\frac{Cl_{89}HCO^{3}_{11}}{Na_{75}Ca_{9}}\,HBO^{2}_{30}\,I_{0.2}\,Br_{1.9}$
e- zhminskii	1	55	9.1	$M_{0.6}\,\frac{Cl_{16}SO^{4}_{37}}{Na_{83}Ca_{14}}\,F_{0.6}\,HBO^{2}_{7}\,HAsO^{4}_{<0.005}$
aiskii	6	52	7.0	$M_{1.3}\,\frac{SO^{4}_{73}Cl_{24}}{Na_{58}Ca_{42}}\,F_{0.9}$

The effects of the petroleum source rock on the composition of Savanskii waters consist of the presence of noticeable quantities of de and bromide, in the absence of sulfate (reduced to hydrogen sul-), and in the microbiological characteristics of the environment in h the bacterial fermenters of hydrocarbons are predominant.

he Nizhne-Chazhminskii spring is near the sea shore, at the hern extremity of the Kronotsk Peninsula. The geologic environ-t at the outcrop of the spring is contingent on the regionally exten- Miocene formations of volcanigenic sediments underlain by the er Paleogene to Lower Neogene Bogachev bed. The Nizhne-zhminskii waters are of the sodium chloride type and they carry tively little germanium: 1 microgram per liter.

he Anavgaiskii spring is in the central part of the Mediam Range edinnyi Khrebet"). According to E. Ehrlich, this spring outdrops zone of a major fissure which controls the Bystraya, Kozyrevskaya, Anavgai Rivers. Geologic environment of this spring includes ogene and Neogene volcanic rocks altered appreciably in the fis- zone wherein the spring is contained. Water of the Anavgaiskii ng is of the sodium sulfate type which is characteristic of mineral- waters developing in Tertiary volcanogenic rocks. Its germanium ent is 6 micrograms per liter.

he available data on germanium in the springs of Kamchatka are ficient for any kind of conclusions regarding the causes respon- for its appearance, its regional distribution, and its association some definite type of water. Only one fact is sufficiently clear, namely, that germanium in waters increases with their temperature notwithstanding certain exceptions. Comparison of our data with so others, on the springs of Japan, is a matter of some interest. Speci cally, the germanium maxima in the Beppu Springs, according to Kavakami [2], are as high as 32 micrograms per liter, while the kn germanium maxima in the springs of Kamchatka are 25 micrograms per liter. Thus the community of the Kamchatka-Kurile and of the Japan mineral water provinces is sustained also by the similarity o the concentrations of germanium they contain.

REFERENCES

1. Mulikovskaya, E. P. Opredelenie Germaniya v Prirodnukh Vodakh (Determination of germanium in natural waters). In press, 1958.
2. Kavakami, Nodzaki, and Koga. Khimicheskoe Izuchenie Goryachikh Istochnikov Beppu (Chemical Studies of the Beppu Hot Springs). *Refer. Zhurn. Khim.* (Journal Chem. Abstracts). *No. 20, 1958.*

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